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CLIMATIC IMPACT ASSESSMENT PROGRAM

JOINT ATMOSPHERIC MODELING
AND CHEMICAL DYNAMICS WORKSHOP

Held at the

NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MARYLAND

12-13 September 1972

Reynold Greenstone, Robert L. Underwood, Editors

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Summary Proceedings

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16. Abstract

On 12-13 September 1972, the Department of Transportation sponsored a joint atmospheric modeling and chemical dynamics workshop. Concerns of the workshop were to establish a chemical kinetics and atmospheric dynamics data base for use in computational models that would be used to assess possible climatic effect due to a projected fleet of high-altitude aircraft. New reaction rate data were reported; models were described; and some predictions of climatic effects were made. Areas needing further work were defined.

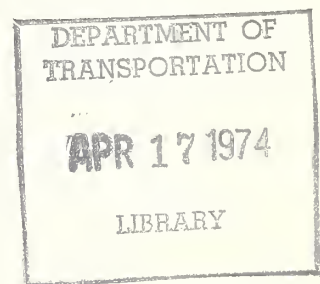| 17. Key Words atmospheric motions, atmospheric chemistry, atmospheric fluid dynamics, computer modeling, climate, ozone, nitric oxide		18. Distribution Statement Unlimited	
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I. INTRODUCTION

A Joint Atmospheric Modeling and Chemical Dynamics Workshop sponsored by the Department of Transportation's (DOT) Climatic Impact Assessment Program (CIAP) was held at the National Bureau of Standards in Gaithersburg on September 12-13, 1972. The workshop was organized by Mr. Reynold Greenstone and Dr. Robert L. Underwood of the DOT/CIAP office. Host to the workshop was Dr. Milton Scheer, Chief of the Physical Chemistry Division of the National Bureau of Standards.

The workshop was divided into two separate panels, a Chemical Dynamics Panel chaired by Dr. Ralph Kummler of Wayne State University and an Atmospheric Modeling Panel chaired by Dr. Thomas D. Taylor of the Aerospace Corporation. Appendix A is a complete list of participants and their affiliations.

The prime objectives of the panels were to review results obtained by the panel members that are pertinent to CIAP objectives; to recommend models that can and should be relied upon in addressing the CIAP problem; to recommend best chemistry data for use by the modelers; and to consider ways to improve the interactions between CIAP modelers and experimenters.

The following sections of this report present (a) highlights of the workshop overall; (b) the chemical dynamics panel report; and (c) the atmospheric modeling panel report. Notes for the chemical dynamics panel report were provided by Dr. Thomas Hard of the Transportation Systems Center who served as rapporteur assisted by Mr. Jerome Pressman of Pressman Enterprises. The report of the panel begins with an overview by the panel chairman, Dr. Kummler. Both notes and an overview of the atmospheric modeling panel were provided by the panel chairman, Dr. Taylor.

II. HIGHLIGHTS OF THE JOINT ATMOSPHERIC MODELING AND CHEMICAL DYNAMICS WORKSHOP

ATMOSPHERIC MODELING

The Atmospheric Modeling Panel reached agreement upon requirements for a model of the wake behind high-altitude aircraft, examined initial studies of important aspects of the dispersion and transport region, and learned details concerning two separate approaches to modeling global-scale circulation. Also, newly initiated studies to investigate the sensitivity of global-circulation models to changes in input data were outlined. Many specific problem areas requiring further attention were identified; these are discussed in the panel report (Chapter IV).

CHEMICAL DYNAMICS

Among the highlights of the chemical dynamics panel were the presentation of new values for certain reaction rate constants, the definition of certain problems that need further attention, the announcement of the availability of O_2 photodissociation computation programs, and an action to coordinate and update results of chemical rate determinations among members of the CIAP chemical dynamics community.

New Values for Reaction Rate Constants

Among those reporting on new rate constant determinations were Scheer of N.B.S., Davis of Maryland, Stuhl of Ford, and Simonaitis of Pennsylvania State University. The reactions involved NO_2, NO, O, O_2, H, OH, HO_2, and CO.

Definition of Problems Needing Further Attention

Among areas needing further work are: further verification of calculations of NO photolysis to confirm that $NO + h\nu \rightarrow N + O$ is an important loss mechanism for NO in the lower mesosphere; resolution of the disagreement by a factor of two for the rate constant for $NO_2 + O \rightarrow NO + O_2$; improvement of $O(^1D)$ rate constants to better than the current factor of two; determination of the quantum yield of $O(^1D)$ from $O_3 + h\nu$ near 3100 A; determination of the rate constant for $NO + HO_2 \rightarrow NO_2 + OH$; determination of the spectral quantum yield of HNO_3 photolysis; and achievement of high-resolution irradiance spectra as a function of altitude, particularly in the 210 nm window

The Availability of O_2 Photodissociation Computation Programs

Both J. Park (Colorado) and R. D. Hudson (NASA) offered to make available their computational programs for O_2 photodissociation.

Coordination of Chemical and Photochemical Rate Data

An agreement was reached between Johnston (U.C. Berkeley) and Garvin (N.B.S.) to institute a program to collect rate data for all chemical and photochemical processes relevant to the CIAP problem. Both Johnston and Garvin will guide this effort with N.B.S. assuming the secretarial role. Individuals with a special concern for reactions involving a particular species were asked to serve as an initial clearinghouse for data on those reactions and then to forward their results to N.B.S.

III. SUMMARY PROCEEDINGS OF THE CHEMICAL DYNAMICS PANEL*
(Ralph Kummler, Chairman)

OVERVIEW AND SUMMARY

The objective of the chemical dynamics workshop was to review the chemistry and photochemistry of the natural and aircraft-perturbed stratosphere. The discussions concerned chemical models; the evaluation of chemical kinetic rate data; laboratory measurements of reaction rates, absorption coefficients, and quantum yields; and solar flux measurements. The program began with reports of work sponsored by the Climatic Impact Assessment Program (CIAP), proceeded to other relevant efforts, and concluded with a discussion of needs.

The following summary of the recommendations of the chemical dynamics panel was presented by panel chairman R. Kummler to a joint meeting with the atmospheric modeling workshop:

1. The set of chemical reactions being reviewed by the CIAP program for determination of their stratospheric relevance is expanding, in order to avoid the omission of any potentially critical processes. However, the objective of the chemical modeling group remains the reduction of the chemical reaction mechanism to the smallest set needed to accurately describe stratospheric chemistry.

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* Dr. Thomas Hard of the DOT Transportation Systems Center prepared this summary proceedings of the chemical dynamics panel with the assistance of Jerome Pressman, Ralph Kummler, and Anthony Broderick. Illustrations and some text were kindly supplied by the speakers.

2. The disagreement by a factor of 2 in measurements of the rate of $NO_2 + O \rightarrow NO + O_2$ at stratospheric temperatures needs to be resolved.

3. According to Brasseur, the predissociation of NO may obviate uncertainties in the downward flux of NO into the stratosphere; because of its importance to the ozone problem, this result should be verified.

4. The quantum yield of $O(^1D)$ in ozone photolysis as a function of wavelength near 310 nm, and the reaction kinetics of $O(^1D)$, are critical problems.

5. The spectral quantum yield of HNO_3 photolysis should be measured.

6. Modelers need <u>absolute</u> irradiance spectra as a function of altitude, particularly in the 210 nm window. High-resolution irradiance spectra also are desirable. At the steep 310 nm absorption edge, flux data obtained with wide-passband filters are probably not helpful.

7. Space and time variations of ozone column and solar irradiance are important, and should be taken into account during the measurement of other photochemical variables.

REVIEW OF JET AND WAKE CHEMISTRY[1]

The present investigation is directed at the nature and extent of chemical reactions in the exhaust jets and wakes of high-altitude aircraft. The object is to determine what reactions might have an important effect on the composition of hot gases as they issue from the engine into the surrounding stratosphere. Experimentally measured exhaust compositions at the exit plane of an engine will not reflect accurately the final chemical composition of the exhaust in the stratosphere if reactions in the wake are important.

The objective of Task I, Problem Definition, is to identify essential features or considerations needed for subsequent development of a wake flow and chemistry model in order to define species concentrations and wake configurations at a time in the wake history when aircraft-induced motions have diminished and are dominated by the natural stratospheric motions. The technical approach for the wake-chemistry portion of

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[1] This material is taken from the presentation by L. B. Anderson of Lockheed, Palo Alto Research Laboratory. It is part of a preliminary draft report to CIAP.

Task I has been to screen the many possible chemical reactions to determine their probable importance in the engine exhaust jet, the near wake, and the far wake — i.e., to as late as 20 min after passage of the aircraft. To examine the reactions in the exhaust jet, however, it has been necessary for the calculations to cover areas even farther upstream — i.e., within the engine nozzle. This has been necessary to examine the rate histories for many of the species before they reach the nozzle exit so that their concentrations at the exit plane can be established. Many atoms and radicals are found to be present, and it cannot be reasonably anticipated that experimental test data on representative turbojet engines will be capable of quantitatively identifying all of the important species. Thus, the engine nozzle kinetics work is a necessary part of the chemical reaction screening process. In this approach, simplifying realtionships have been sought, such as steady state and partial equilibrium relationships among minor species, to discover when such relationships can be used for making reliable predictions. The reliability of the simplifying methods is ascertained by comparison of the results with fully coupled computer solutions of the reacting flow problem.

FIGURE 1
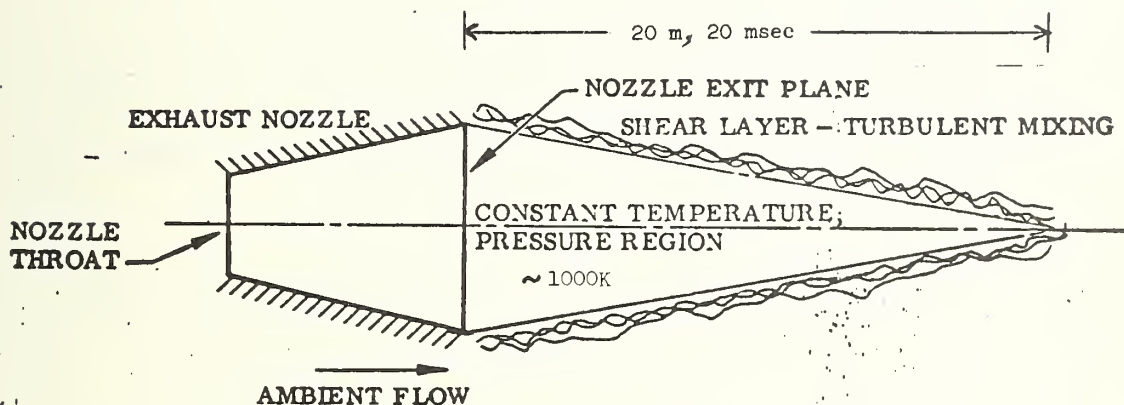
Near Jet Exhaust

The emphasis in final development of the chemistry model will be influenced by the interface with and requirements of the chemical modeling program for the post-wake dispersion regime. It is anticipated that the NO_x concentrations and total NO_x will be first on the list of priorities. It is anticipated that any significant conversion of NO_x in the wake to HNO_3 will be of major interest. Formation of sulfate aerosol in the wake and diffusion and transport regime will also be of interest. It seems likely that the diffusion and transport regime and subsequent climatic analyses will be less sensitive to uncertainties in wake CO and hydrocarbon levels than to NO_x concentration. In light of this, a simplified wake-chemistry model may serve nicely. If, on the other hand, detailed information on minor wake species, exhaust generated radicals, etc., is required, a much more general and comprehensive wake kinetics model will be needed.

The scope of the chemical screening process is broad; i.e., thermochemical reactions, photochemistry, and particulate generating reactions are all considered. Because oxides of nitrogen are thought to play a particularly important role in the stratosphere, their reactions are given special attention, and analysis of the photochemical catalytic NO_x and ozone histroy following passage of an aircraft through the stratosphere is carried out to times well beyond the 20-min "end to wake" time.

For studies of thermal reactions in the engine exhaust regime, the analytical approach involves setting up a chemical kinetics model using those elementary reactions that play a role in changing the concentrations of engine emissions in the exhaust nozzle and the near jet downstream from the engine exit plane. Numerical methods are used to integrate the resulting governing chemical rate equations up to the point where the exhaust flow mixes with the ambient atmosphere. Initial conditions for the computations are compatible with available data on engine exhaust composition.

In particular, reactions affecting the oxidation of CO to CO_2 and NO to NO_2, as well as conversion of NO_2 to HNO_3, are of interest. A model consisting of elementary forward and backward reactions pertinent to these exhaust chemical systems has been used in this study. Reaction rate constants are taken from recent evaluations available in the literature. The fluid-dynamic structure of the exhaust jet region was obtained from analytical predictions and experimental data available from the literature.

TABLE 1

CHEMICAL REACTIONS IN THE $CO_x/NO_x/AIR$ SYSTEM

Reaction Number	Reaction	Reaction Rate Variables*			Ref.
		A	n	E	
1	$H + N_2O = N_2 + OH$	3.01×10^{13}	0	10,800	3-15
2	$N + OH = NO + H$	4.21×10^{13}	0	0	3-15
3	$O + N_2O = N_2 + O_2$	3.61×10^{13}	0	24,000	3-16
4	$N_2 + NO_2 = NO + N_2O$	1.41×10^{14}	0	83,000	3-16
5	$H + NO_2 = NO + OH$	7.25×10^{14}	0	1,930	3-17
6	$HO_2 + NO = OH + NO_2$	6.00×10^{11}	0	0	3-63
7	$O + N_2 = NO + N$	1.44×10^{14}	0	75,580	3-16
8	$NO + O = N + O_2$	4.10×10^{9}	0	38,340	3-16
9	$M + NO_2 = O + NO + M$	1.10×10^{16}	0	65,000	3-16
10	$NO + O_2 = O + NO_2$	3.05×10^{12}	0	47,400	3-16
11	$NO + NO = N_2O + O$	7.05×10^{11}	0	65,000	3-16
12	$M + N_2O = N_2 + O + M$	6.30×10^{14}	0	56,800	3-16
13	$CO + OH = CO_2 + H$	4.20×10^{11}	0	1,080	3-4
14	$H + O_2 = OH + O$	2.20×10^{11}	0	16,800	3-18
15	$OH + OH = H_2O + O$	6.30×10^{12}	0	1,100	3-18
16	$O + H_2 = H + OH$	1.80×10^{10}	1	8,900	3-18
17	$H_2 + OH = H_2O + H$	2.20×10^{13}	0	5,150	3-18
18	$M + H_2 = H + H + M$	2.20×10^{14}	0	96,000	3-18
19	$M + H + OH = H_2O + M$	1.40×10^{23}	-2	0	3-18
20	$M + O_2 = O + O + M$	2.50×10^{18}	-1	118,500	3-17
21	$M + H + O_2 = HO_2 + M$	1.50×10^{15}	0	-1,000	3-18
22	$H + HO_2 = OH + OH$	2.50×10^{14}	0	1,900	3-18
23	$OH + HO_2 = H_2O + O_2$	1.20×10^{14}	0	0	3-64
24	$O + HO_2 = OH + O_2$	5.00×10^{13}	0	1,000	3-18
25	$H + HO_2 = H_2 + O_2$	2.50×10^{13}	0	700	3-18
26	$H + HO_2 = H_2O + O$	1.00×10^{13}	0	1,000	3-18
27	$NO_2 + OH = HNO_3$	2.90×10^{12}	0	0	3-19

*Reaction rate constant $k = A T^n \exp(E/RT)$.

TABLE 2

CHEMICAL KINETIC SITUATION TWO METERS DOWNSTREAM OF NOZZLE EXIT PLANE

	REACTION $\sum_i \nu_i A_i \rightleftharpoons \sum_j \nu_j A_j$	FORWARD RATE CONSTANT k^f	FORWARD REACTION RATE $r^f = k^f \prod_i [A_i]^{\nu_i}$	NET REACTION RATE $r^f - k^r \prod_j [A_j]^{\nu_j}$	COMMENTS*
1	$H + N_2O \rightleftharpoons N_2 + OH$	1.01 E+11	1.57 E-12	1.57 E-12	F
2	$N + OH \rightleftharpoons NO + H$	4.21 E+13	3.21 E-17	-3.63 E-17	B
3	$O + N_2O \rightleftharpoons N_2 + O_2$	1.14 E+8	1.39 E-15	1.39 E-15	F·
4	$N_2 + NO_2 \rightleftharpoons NO + N_2O$	1.35 E-5	1.94 E-26	-7.46 E-21	R
5	$H + NO_2 \rightleftharpoons NO + OH$	2.62 E+14	1.86 E-10	1.86 E-10	F
6	$HO_2 + NO \rightleftharpoons OH + NO_2$	1.25 E+11	1.51 E-11	1.51 E-11	F
7	$O + N_2 \rightleftharpoons NO + N$	6.93 E-4	7.69 E-20	-3.66 E-17	R
8	$NO + O \rightleftharpoons N + O_2$	6.73 E+0	3.30 E-19	1.78 E-19	B
9	$NO_2 + M \rightleftharpoons NO + O + M$	1.41 E+1	2.72 E-20	-1.75 E-10	R
10	$NO + O_2 \rightleftharpoons O + NO_2$	4.20 E+1	3.93 E-16	-4.01 E-12	R
11	$NO + NO \rightleftharpoons N_2O + O$	9.01 E-4	5.06 E-23	-1.94 E-16	R
12	$N_2O + M \rightleftharpoons N_2 + O + M$	6.09 E+1	2.56 E-16	-4.42 E-14	R
13	$CO + OH \rightleftharpoons CO_2 + H$	3.17 E+11	2.32 E-8	1.85 E-8	B
14	$H + O_2 \rightleftharpoons OH + O$	3.11 E+10	3.28 E-7	-2.30 E-9	FASTEST REACTION BUT VERY NEAR PE
15	$OH + OH \rightleftharpoons H_2O + O$	3.53 E+12	5.91 E-8	-8.48 E-12	PE
16	$O + H_2 \rightleftharpoons H + OH$	1.57 E+11	8.06 E-9	9.74 E-10	NEAR PE
17	$H_2 + OH \rightleftharpoons H_2O + H$	1.45 E+12	4.65 E-8	5.63 E-9	NEAR PE
18	$H_2 + M \rightleftharpoons H + H + M$	2.22 E-8	3.96 E-24	-2.26 E-10	R
19	$H + OH + M \rightleftharpoons H_2O + M$	1.54 E+17	3.80 E-9	3.78 E-9	F
20	$O_2 + M \rightleftharpoons O + O + M$	1.85 E-12	5.26 E-26	-3.46 E-12	R
21	$M + H + O_2 \rightleftharpoons HO_2 + M$	2.54 E+15	1.91 E-8	1.91 E-8	F
22	$H + HO_2 \rightleftharpoons OH + OH$	9.175 E+13	1.24 E-8	1.24 E-8	F
23	$OH + HO_2 \rightleftharpoons H_2O + O_2$	5.90 E+12	3.90 E-10	3.90 E-10	F
24	$O + HO_2 \rightleftharpoons OH + O_2$	2.95 E+13	3.12 E-9	3.12 E-9	F
25	$H + HO_2 \rightleftharpoons H_2 + O_2$	1.73 E+13	2.34 E-9	2.34 E-9	F
26	$H + HO_2 \rightleftharpoons H_2O + O$	5.90 E+12	7.98 E-10	7.98 E-10	F
27	$NO_2 + OH \rightleftharpoons HNO_3$	2.90 E+12	1.00 E-12	-1.62 E-17	PE

*F — FORWARD REACTION DOMINATES.
R — REVERSE REACTION DOMINATES.
PE — FORWARD RATE = REVERSE RATE, REACTION IN PARTIAL EQUILIBRIUM.
B — BOTH FORWARD AND BACK RATES SIGNIFICANT AND NONEQUAL.

In particular, reactions affecting the oxidation of CO to CO_2 and NO to NO_2, as well as conversion of NO_2 to HNO_3, are of interest. A model consisting of elementary forward and backward reactions pertinent to these exhaust chemical systems has been used in this study. Reaction rate constants are taken from recent evaluations available in the literature. The fluid-dynamic structure of the exhaust jet region was obtained from analytical predictions and experimental data available from the literature.

The major conclusions reached in the investigation are as follows:

- In an afterburning engine, nonequilibrium effects are an important aspect of the chemistry in the engine exhaust expansion nozzle and exhaust jet regime. There is substantial oxidation of CO to CO_2 in the nozzle and jet, and the concomitant production of H atoms maintains the concentrations of H, O, and OH well above their equilibrium values. These nonequilibrium concentrations persist from the exhaust jet out to the regions where the jet mixes with the ambient atmosphere, as shown in Figure 2.

- Oxidation of NO to NO_2 is not a significant factor in the exhaust regime. The NO_2/NO ratio is maintained well below its equilibrium value ($\sim 10^{-3}$) by fast reactions such as the following:

$$NO_2 + H \rightarrow NO + OH$$

$$NO_2 + M \rightarrow NO + O + M$$

$$NO_2 + O \rightarrow NO + O_2$$
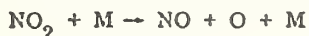
- Although OH concentrations are high in the jet, the small NO_2 concentration in the exhaust region prevents significant formation of HNO_3 from the reaction

$$NO_2 + OH \rightarrow HNO_3$$

- In ground tests the exhaust gases are maintained at substantially higher temperatures for longer residence than at high altitude. As observed, the chemical kinetics model predicts the occurrence of significantly more CO oxidation in the exhaust jet for an engine under static test conditions at sea level, than it predicts for stratospheric flight.

- The subject of chemical kinetics in turbulent flows is considered. To a large extent, chemistry is found to be "diffusion limited" in the exhaust jet core and "reaction rate limited" in the wake. The simple, "well mixed" kinetics model, which ignores diffusion and turbulence in the exhaust jet, appears to agree reasonably well with ground-test data on CO profiles. This may mean that the net influence of turbulence on the chemistry is small.
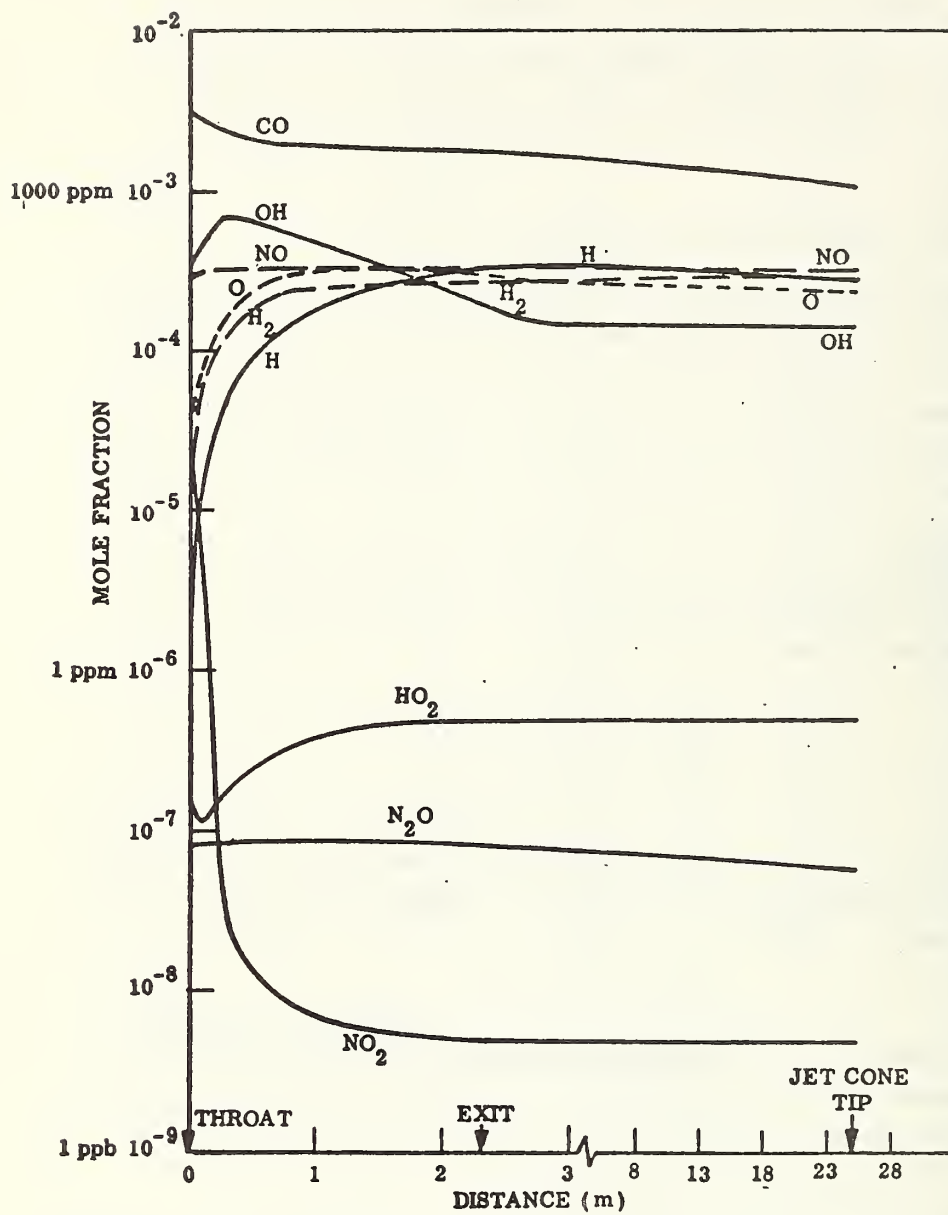
Fig. 2. Centerline Concentration Profiles for GE-4 at Maximum Power

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- In the exhaust jet, ratios between H, .O, and OH appear to be nearly constant, independent of elapsed time. Effects tending to alter the ratios, such as O-atom removal by methane, appear to be small. This allows steady-state approximations to be used for HO_2/OH, NO_2/NO, and SO_3/SO_2 ratios, which are small.

- In the jet mixing region and the near wake, the possibility of aerosol formation by the following reaction pair cannot be ruled out:

$$SO_2 + O + M \rightarrow SO_3 + M$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
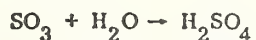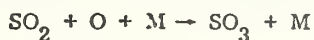
The magnitude of the effect is expected to be highly dependent on the specific cooling and dilution rate histories involved. All other reactions that might lead to particulate formation appear to be too slow to contribute significantly in the wake regime.

- Addition of unburned exhaust hydrocarbons to the stratosphere does not appear to be significant. Catalytic chain effects of hydrocarbons on ozone/NO_x cycles degrade the hydrocarbons and are unimportant. Removal of NO_x by hydrocarbons in the stratosphere is an important area for study, but the contribution from engine exhaust hydrocarbons is dwarfed by the ambient methane.

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REVIEW OF CHEMICAL DYNAMICS FROM THE DIFFUSIVE TRANSPORT SCALE TO THE GLOBAL SCALE [2]/

I. ASILOMAR STATUS

A. Data

- List of Chemical and Photochemical Reaction Processes - Partially Ordered For Importance and Directed Mainly at O_3.

- Preliminary Estimate of Uncertainties in Rate Coefficients for Sensitivity Studies

- No Comprehensive, Up To Date, Compendium of Evaluated Atmospheric Reaction Rate Constants.

- Recommendations for Additional Laboratory Work.

- Recommendations for Updated Atmospheric Composition, Solar Flux, and Optical Data.

B. Models

Operate, to date, upon simplified forms of the more general set of kinetic equations:

$$\frac{\partial C_i}{\partial t} + \vec{v} \cdot \vec{\nabla} C_i = F_i(\vec{C}) - R_i(\vec{C})C_i + S_i(\vec{x},t) + H_i(\vec{x},t) \quad , \qquad (1)$$

where $C_i \equiv C_i(\vec{x},t)$ is the mean concentration of species i at position $\vec{x}$ and time t,
$\vec{V} \equiv \vec{V}(x,t)$ is the velocity

$\vec{F}_i(\vec{C}) \equiv$ local production rate by chemical and photochemical reactions

$R_i(\vec{C})C_i \equiv$ local destruction rate by chemical and photochemical
 reactions

$S_i(\vec{x},t) \equiv$ local net source term

$H_i(\vec{x},t) \equiv$ terms representing departures from mean variables

Classes of Models Receiving Majority of Attention at Asilomar

- $$\frac{\partial C_i}{\partial t} = F_i(C) - R_i(C)C_i + S_i(t) \tag{2}$$
  (often set $\partial C_i/\partial t = 0$ and/or $S_i(\vec{x},t) = 0$)

- $$\vec{v} \cdot \vec{V} \, C_i = F_i(\vec{C}) - R_i(\vec{C})C_i \quad \text{(one-dimension)} \tag{3}$$

  $$\frac{\partial C_i}{\partial t} + \vec{v} \cdot \vec{V} \, C_i = S_i(\vec{x},t) + H_i(\vec{x},t)$$
  $$\text{(one, two, or three dimension) (4)}$$
  (often set $S_i(\vec{x},t) = 0$ and/or $H_i(\vec{x},t) = 0$)

- Mechanism Modelling Operates on Sets of Chemical and Photochemical
  Reactions to be included in $F_i(\vec{C}) - R_i(\vec{C})C_i$ Terms.

- Inhomogeneous Chemical Modelling Places Emphasis Upon $H_i(\vec{x},t)$ terms

C. Standard Atmosphere and Solar Fluxes

- U.S. Standard Atmosphere ρ, p, T vs. z

- concentrations of minor species vs. z badly lacking for NO, NO_2,
  sulfur compounds, and other minor species which may possibly
  absorb from 1700 Å - 3000 Å

- microscopic absorption cross sections, $\sigma_a(\lambda, p, T)$ - many lacking
  high resolution, particularly in line wings

  e.g. O_2 - Schumann-Runge Bands

  NO - Bands

- solar flux outside earth's atmosphere lacks resolution to, say, 1 Å

- solar flux vs. altitude - a number of routines internal to model
  codes exist - apparently none incorporate high resolution data for
  O_2 Schumann-Runge bands of Ackerman, et al. The reduction factors
  Kockarts are not particularly useful for general modelling needs.

D. Aerosols

. Major concerns are

   i) Radiative properties

   ii) Surface chemistry - effect on stratospheric chemistry
   directly because of capacity as sinks

. Qualitative considerations exceed quantitative work, to date

II. DEVELOPMENT SINCE ASILOMAR

A. Data

. Chapman reaction rates improved

. NBS updating earlier compendium of evaluated atmospheric
rate constants (numerous evaluators included)

   NBS considers only evaluated data

. LLL, in cooperation with NBS and individual users, maintaining
compendium of evaluated data and other data being used by
various modellers (particularly in absence of evaluated rates).
LLL states what they are using in LLL codes at a given time
for radiative and chemical rate data.

. Much of hierarchy in Asilomar table 3.1 has been documented
with regard to data sources and data values with uncertainties.

   Also "consistency flagging" is underway for sensitivity
   studies.

B. Models

. $$\frac{\partial C_i}{\partial t} = F_i(\vec{C}) - R_i(\vec{C})C_i + S(t) \tag{5}$$

   with   i) current evaluated data

       ii) high resolution (in Schumann-Runge bands), time-
       dependent solar flux

      iii) time varying sources

       iv) completely general solution method for stiff systems

. $$\int d^3x \left[\frac{\partial C_i}{\partial t} + \vec{\nabla} \cdot \vec{V} \, C_i \right] = \int d^3x \left\{ F_i(\vec{C}) - R_i(\vec{C})C_i \right\} \tag{6}$$

   with   i) local (x,t) solar fluxes

       ii) current evaluated data

3—12

- most significant development is formulation of dynamic, kinetic models (one space dimension)

$$\frac{\partial C}{\partial t} + \vec{v} \cdot \vec{\nabla} C_i = F_i(\vec{C}) - R_i(\vec{C}) C_i + S_i(\vec{x}, t) \qquad (7)$$

  this development represents an emergence from an era of exceedingly macroscopic models which required massive phenomenological inter-pretation for detailed (or local) information.

- Likely directions for future efforts brought about by dynamic-kinetic modelling will be discussed in Section III.

C. Standard Atmosphere and Solar Flux

- Are a number of routines, which can calculate solar flux for arbitrary time, altitude, latitude, and longitude; given column densities of minor constituents and standard atmospheric profile. for major constituents-particularly O_2. At least one routine has high resolution of Schumann-Runge bands (from data of Ackerman, et al).

- Is ongoing theoretical and experimental work to improve treatment of line profiles in O_2 bands. This could possibly be significant effect in transparency.

III. UPDATING OF NEEDS

A. Data

- numerous needs in chemical rate constants - specific reactions evident in compendia and Asilomar proceedings

  i) low temperature data needed for large no. of reactions

  ii) more precise data needed for many reactions - greatest priority attached to reactions most affecting odd oxygen and to reactions associated with stratospheric sink mechanisms for species affecting odd oxygen

- radiative data

  i) need more resolution in absorption cross-sections, $\sigma_a(\nu)$ and especially in quantum yields, Q_ν

  ii) need temperature and pressure dependence of $\sigma_a(\nu)$, especially in bands.

  iii) need better treatment, theoretically and experimentally of line profiles, especially in wings of lines (already mentioned for solar fluxes)

  iv) only limited evaluation, to date

B. Models

- sensitivity to space and time dependent diffusion coefficients, sources, and net removal processes (sinks) can be as great as sensitivity to major catalytic cycles in dynamic-kinetic model.

- the above point can create a situation where weak mechanisms in the reaction rate hierarchy take on significance of major catalytic cycles if the weak mechanism is associated with a removal process for something like NO - thus may need to adjust our existing interpretation of a reaction hierarchy to accommodate coupled dynamic-kinetic mechanisms.

- the above points amplify need to understand chemistry of aerosols as sinks for important species

- the above points amplify the need for more accurate determinations of NO, O_3, and NO_2 profiles with seasonal variations as well as for better knowledge of specific source and removal agents.

- all of the considerations so far advanced for ozone kinetics and dynamics should extend to encompass the other species and solar spectral regions associated with earth's energy budget.

CHEMICAL MODEL PRESENTATIONS

The following paragraphs summarize the presentations of several chemical modelers at the joint session of the atmospheric model and chemi · dynamics panels.

G. Brasseur (Institute of Aeronomy, Brussels)

Subjects covered were the aeronomy of NO and NO_2, including pr dissociation of NO. A line-by-line calculation in the NO δ-bands, made necessary by the overlying O_2 Schumann-Runge bands, seems to result in · net source of NO above the stratosphere.

E. Hesstvedt (University of Oslo, Norway)

Hesstvedt described a model with ozone, water vapor, and nitroge · oxide chemistry coupled with vertical and meridional transport. His abstrac follows:

A theoretical meridional model of the O_3 layer is presented. Two-dimensional transport by eddies and mean motion is considered together with photochemical reactions involving O, N, and H. The model is used to evaluate the effect of increased contents of H_2O and of NO_x in the stratosphere. It is found that a doubling of stratospheric humidity will reduce the total amount of O_3 by less than 1%, while a doubling of NO_x will result in an 18% reduction for middle latitudes and summer. A 10% increase in NO_x will reduce the total O_3 by about 2.8%. The relation between UV radiation and total O_3 is described, in particular, for wavelengths of biological interest (290 to 320 nm). A 1% decrease in total O_3 will result in a 2% increase in erythemogenic UV radiation.

J. Chang (Lawrence Livermore Laboratory)

Chang discussed the derivation of vertical transport from chemistry, and vice versa. In a one-dimensional ozone chemical model, he has inserted the stratospheric NO_x injection recently estimated by Foley and Ruderman for the 1961-62 atmospheric nuclear weapons test series. He finds that the effect is spread over a period of about three years, with a peak reduction of 8% of the total ozone column occurring about a year after the tests. This suggests that the 1960-66 ozone data require more careful statistical analysis to detect possible effects on the ozone of NO_x from nuclear weapons tests.

T. Shimazaki (NOAA, Boulder)

Shimazaki described work on a two-dimensional photochemical model. This model was originally developed for the mesosphere, and is now being modified for the much longer characteristic times of stratospheric chemistry.

J. London (University of Colorado)

London described preliminary work on a photochemical model, with three-dimensional transport provided by the NCAR circulation model of Kasahara, Washington, and Sasamori.

H. Johnston (U.C. Berkeley)

Johnston described his study of the global stratospheric ozone budget. He showed that ozone is produced by $O_2 + h\nu \rightarrow O + O$, followed by $O + O_2 + M \rightarrow O_3 + M$, much faster than it can be destroyed by $O + O_3 \rightarrow O_2 + O_2$ or by transport to the troposphere. Small amounts of NO_x can account for the deficit, and the distribution of NO_x is as important as its amount.

EVALUATION OF CHEMICAL KINETICS RATE DATA

D. Garvin reviewed the achievements and plans of the N.B.S. evaluation team, relative to the list of reactions assembled at the Asilomar Conference. He also described a time-shared kinetics data system that could provide modelers with the most recent measurements and evaluations of reaction rates. The system was demonstrated during this meeting. It would cost N.B.S. about $1,000 per year to maintain, and would cost the user between $6 and $15 per hour of connect time. Garvin's notes follow:

TABLE 3
CIAP RATE DATA SUMMARY

Table 3a. Summary of Status of Asilomar List

Symbol*	Present Status	No.**
12-	Some Recommendation Available	31
-12 P12	NBS Plans for Fall 72 and 73	15
?12	Other Reactions (Estimates Feasible)	5
12	Major Problems Using Existing Data	12
		63
* Marks next to reaction number on attached list. ** Each reaction is counted only once – in the first category in which it appears.		

Table 3b. NBS Data Sheets

	Total	Asilomar
Issued 1972	28	(13)
To Be Issued Fall 72	14	(10)
Plans for 1973	13	(6)
	55	(29)

TABLE 4. REACTIONS AND CONFIDENCE LIMITS
FOR THEIR RATE CONSTANTS

Reaction No.	Reaction	Confidence Statement
	I. Basic Chapman Mechanism	
→1	$O_2 + h\nu \rightarrow O + O$	$\sigma \pm 20\%$
‐‐2‐	$O + O_3 \rightarrow O_2 + O_2$	k well known
P 3‐	$O + O_2 + M \rightarrow O_3 + M$	k well known
→4‐	$O_3 + h\nu \rightarrow O(^1D) + O_2$	$\sigma \pm 10\%$
	II. Destruction of Odd-Oxygen by NO_x	
‐5‐	$NO + O_3 \rightarrow NO_2 + O_2$	$k \pm 20\%$
‐6	$NO_2 + h\nu \rightarrow NO + O$	$\sigma, J \pm 20\%$
‐7‐	$NO_2 + O \rightarrow NO + O_2$	$k + 20, -50\%$
	III. Removal of NO_x	
P 8	$OH + NO_2 \xrightarrow{M} HNO_3$	k factor of 2, function of pressure
‐9‐	$OH + HNO_3 \rightarrow H_2O + NO_3$	k factor of 2
‐10‐	$HNO_3 + h\nu \rightarrow H + NO_3$	σ factor of 100
‐11‐	$\rightarrow OH + NO_2$	
	IV. NO Production	
‐12‐	$N_2O + O(^1D) \rightarrow NO + NO$	k factor of 2
‐13‐	$\rightarrow N_2 + O_2$	k factor of 2
P 14	$N_2O + h\nu \xrightarrow{\sigma_I} N_2 + O(^1D)$	$\sigma_I \pm 20\%$
	IV.A. Hypothetical Reaction Affecting NO	
P 15	$N_2O + h\nu \xrightarrow{\sigma_{II}} N + NO$	Important if $\sigma_{II} = .01$ $\sigma (N_2O + h\nu \rightarrow N_2 + O)$
⑯	$N_2(A) + O \rightarrow NO + N$	
‐17‐	$O(^1D) + M \rightarrow O(^3P)' + M$	$O(^3P)'$ indicates hot $O(^3P)$
⑱	$M + O(^3P)' + N_2 \rightarrow N_2O^\bullet + M$	$N_2O^\bullet$ indicates excited N_2O
⑲	$N_2O^\bullet \rightarrow NO + N$	
⑳	$\rightarrow N_2 + O$	
㉑	$\rightarrow N_2O$	
㉒	$O(^1D) + N_2 \rightarrow N_2O^\bullet$	Slow
	V. Higher Oxides of Nitrogen	
‐23‐	$NO_2 + O_3 \rightarrow NO_3 + O_2$	k factor of 10^4 uncertainty at stratospheric T depending on activation energy $= 7 \pm 2$ kcal.
? 24	$NO_3 + h\nu \rightarrow NO + O_2$	$\sigma, J \pm 20\%$ at peak (6200A) ϕ factor of 10
? 25	$NO_3 + h\nu \rightarrow NO_2 + O$	σ small at peak, possibly important at lower wavelength

σ - Photochemical absorption cross section
k - Reaction rate constant

TABLE 4 (Cont)

V. Higher Oxides of Nitrogen (Cont.)

Reaction	Notes
$NO_2 + NO_3 \rightarrow N_2O_5^*$	$k \pm 20\%$
$N_2O_5^* \rightarrow NO_2 + NO_3$	
$\rightarrow N_2O_5$	
$N_2O_5 + h\nu \rightarrow$	
$N_2O_5 + O \rightarrow$	Products unknown, being worked on
$N_2O_5 + OH \rightarrow$	
$N_2O_5 + HO_2 \rightarrow$	
$N_2O_5 + H_2O \rightarrow$	Slow in gas phase

VI. $O(^1_D)$ and O_3

Reaction	Notes
$O(^1_D) + O_3 \rightarrow O_2 + O_2$	
$O(^1_D) + M \rightarrow O(^3_P) + M$	

VII. Reactions Affecting OH, HO_2

Reaction	Notes
$OH + O \rightarrow H + O_2$	k factor of 2
$H + O_2 + M \rightarrow HO_2 + M$	k factor of 2; probably only important H reaction
$HO_2 + O \rightarrow OH + O_2$	k not known
$OH + O_3 \rightarrow HO_2 + O_2$	k factor of 10^3
$OH^\dagger + O_3 \rightarrow H + O_2 + O_2$	k depends on vibrational T; † indicates vibrational excitation
$OH + CO \rightarrow CO_2 + H$	k factor of 2
$O(^1_D) + H_2O \rightarrow OH + OH$	k factor of 2
$O(^1_D) + CH_4 \rightarrow CH_3 + OH$	k factor of 2
$O(^1_D) + H_2 \rightarrow OH + H$	k factor of 2
$OH + HO_2 \rightarrow H_2O + O_2$	k of 2×10^{-10} seems high
$OH + OH \rightarrow H_2O + O$	k factor of 2
$H + O_3 \rightarrow OH^\dagger + O_2$	k factor of 2
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	k factor of 2
$H_2O_2 + h\nu \rightarrow OH + OH$	σ factor of 2
$H_2O_2 + O \rightarrow HO_2 + OH$	k factor of 2
$H_2O_2 + OH \rightarrow H_2O + HO_2$	k factor of 2
$HO_2 + NO \rightarrow OH + NO_2$	k probably high
$HO_2 + CO \rightarrow OH + CO_2$	k low, factor of 10
$OH + CH_4 \rightarrow H_2O + CH_3$	k factor of 2
$OH + H_2 \rightarrow H_2O + H$	k factor of 2
$OH + h\nu \rightarrow O + H$	σ very uncertain
$HO_2 + h\nu \rightarrow H + O_2$	σ very uncertain
$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	
$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2$	
$CH_3O + O_2 \rightarrow CH_2O + HO_2$	
$CH_2O + OH \rightarrow HCO + H_2O$	k factor of 2
$HCO + O_2 \rightarrow CO + HO_2$	k high; uncertain but sufficient

TABLE 5.

NBS Chemical Kinetics Data Survey

I. Evaluations of Rate Constants and Photochemistry
    Published in NBS Reports 10692 and 10828

A $O + O_3 \rightarrow 2O_2$ $HNO_2 + H \rightarrow$ products

    $O_2(^1\Delta_g) + M \rightarrow O_2 + M$ $HNO_2 + HO \rightarrow H_2O + NO_2$

    $O_2(^1\Sigma_g^+) + M \rightarrow O_2 + M$ $HNO_2 + O \rightarrow HO + NO_2$

A $O_3 + h\nu$ (u.v.) $HNO_3 + H \rightarrow HO + HNO_2$

    $O_3 + h\nu$ (visible) $HNO_3 + HO \rightarrow H_2O + NO_3$ A

A $H + O_3 \rightarrow HO + O_2$ $HNO_3 + O \rightarrow HO + NO_3$

A $HO + O_3 \rightarrow$ products $HNO_3 + h\nu$ A

A $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ $H + NO_2 \rightarrow HO + NO$

A $H_2O + O(^1D) \rightarrow 2HO$ $H_2O + NO + NO_2 \rightarrow 2HNO_2$

A $H_2O_2 + h\nu$ $H_2O + N_2O_5 \rightarrow 2HNO_3$ A

A $NO + O_3 \rightarrow NO_2 + O_2$ $H_2O_2 + NO \rightarrow$ products

    $NO_2 + O + M \rightarrow NO_3 + M$

    $NO_2 + O_3 \rightarrow NO_3 + O_2$

A $N_2O + O(^1D) \rightarrow N_2 + O_2$

A $\rightarrow 2NO$

    $HNO + H \rightarrow H_2 + NO$

    $HNO + HO \rightarrow H_2O + NO$
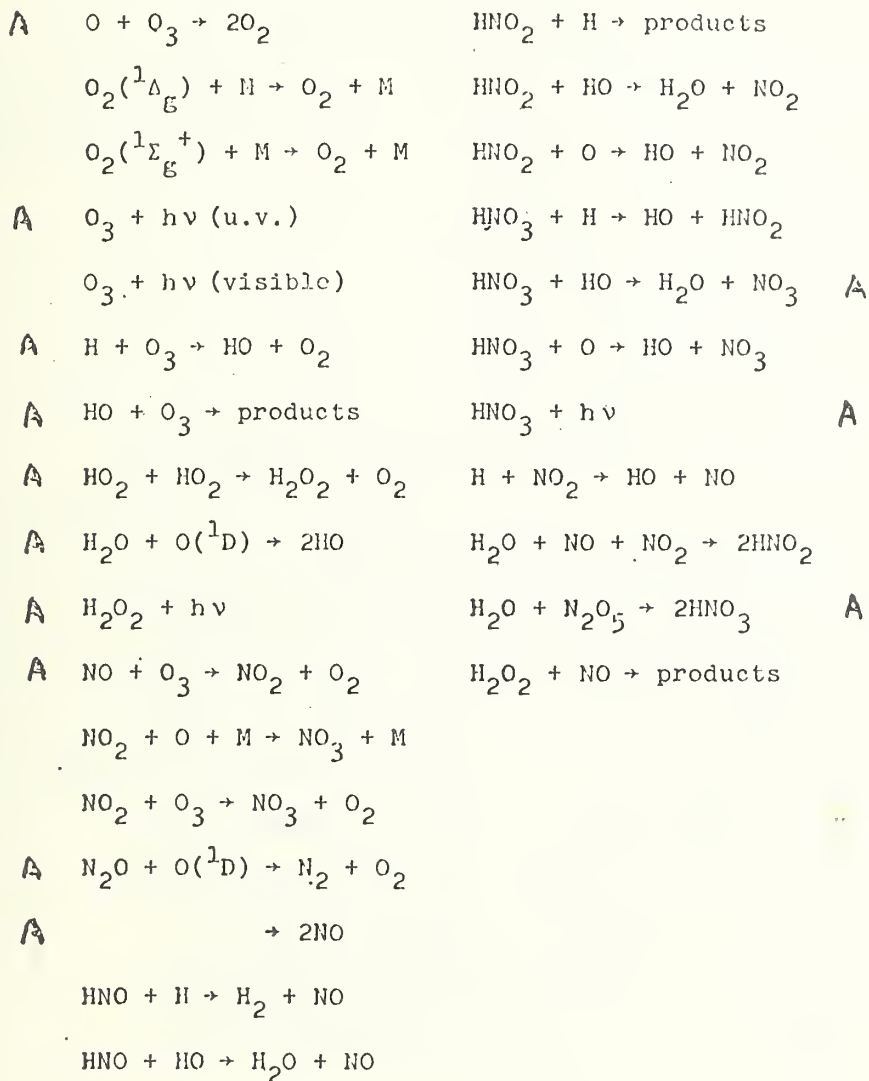
A = Asilomar list

TABLE 5 (Cont)

II. Evaluations of Kinetics and Photochemical Data
     to be issued, Fall 1972.

$$O_2 + M \rightarrow 2O + M$$

$$H_2O_2 + H \rightarrow$$

A $H_2O_2 + HO \rightarrow HO_2 + H_2O$

A $NO_2 + O \rightarrow NO + \dot{O}_2$

A $O_2 + h\nu$

$NO + h\nu$

A $NO_2 + h\nu$

A $N_2O_5 + h\nu$

$HNO_2 + h\nu$

A $O(^1D) + M,$

$$M = O_2, \ N_2, \ O_3, \ H_2, \ CH_4, \ (N_2O, \ H_2O)$$
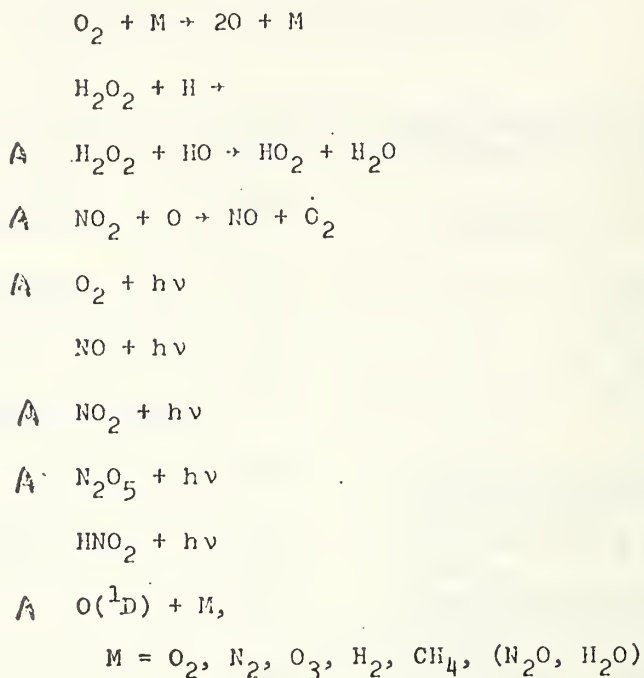
III. Rate Evaluations Planned for 1973

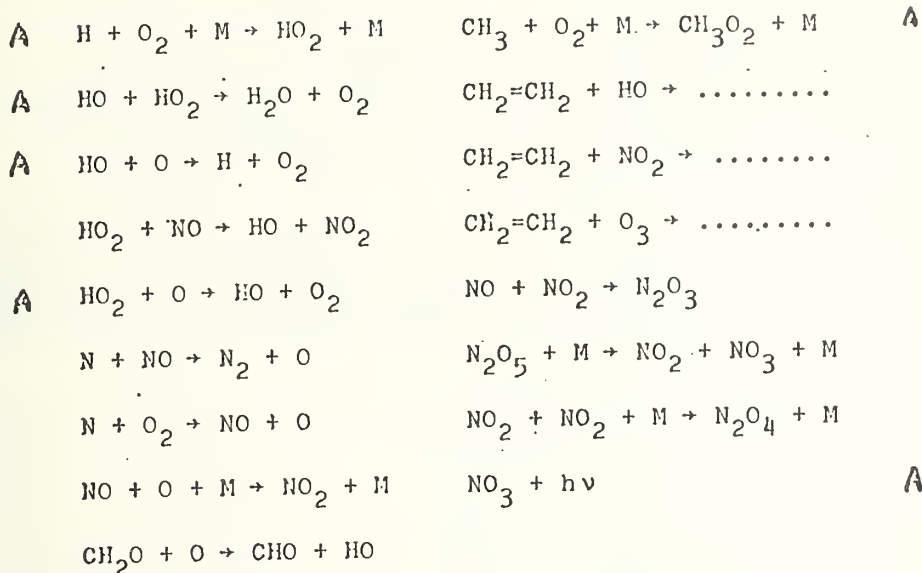A $O + O_2 + M \rightarrow O_3 + M$ $HO_2 + HO_3 \rightarrow NO + NO_2 + O_2$

A $O + N_2O_5 \rightarrow \ \dotsc\dotsc$ $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

$O + CH_2{=}CH_2 \rightarrow$ $NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$

$H_2O + h\nu \rightarrow H + HO$ $NO + NO_3 \rightarrow NO_2 + NO_2$

A $N_2O + h\nu \rightarrow N_2 + O(^1D)$ $HO + NO_2 + M \rightarrow HNO_3 + M$ A

A $\rightarrow N + NO$ $CHO + O_2 \rightarrow CO + HO_2$ A

$CH_2O + h\nu \rightarrow CHO + H$ $CO + HO_2 \rightarrow CO_2 + HO$
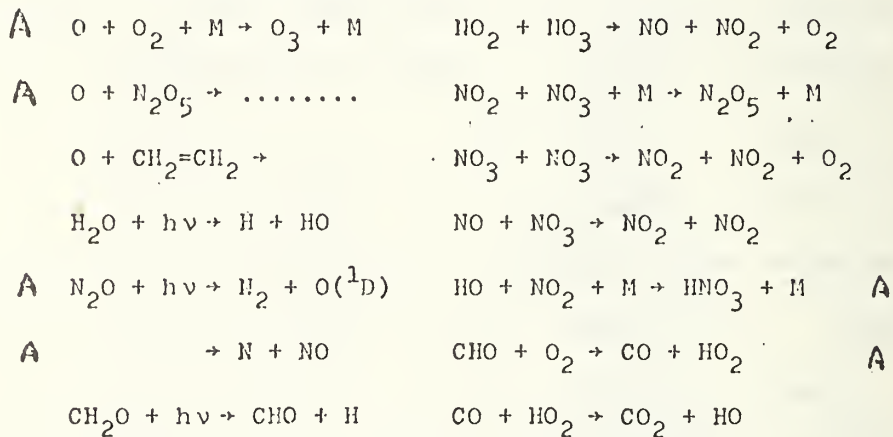
A = Asilomar list

TABLE 5 (Cont)

IV. Other Possibilities. Evaluate or Validate Existing
     Evaluation

A $H + O_2 + M \rightarrow HO_2 + M$ $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ A

A $HO + HO_2 \rightarrow H_2O + O_2$ $CH_2=CH_2 + HO \rightarrow \ldots\ldots$

A $HO + O \rightarrow H + O_2$ $CH_2=CH_2 + NO_2 \rightarrow \ldots\ldots$

   $HO_2 + NO \rightarrow HO + NO_2$ $CH_2=CH_2 + O_3 \rightarrow \ldots\ldots$

A $HO_2 + O \rightarrow HO + O_2$ $NO + NO_2 \rightarrow N_2O_3$

   $N + NO \rightarrow N_2 + O$ $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$

   $N + O_2 \rightarrow NO + O$ $NO_2 + NO_2 + M \rightarrow N_2O_4 + M$

   $NO + O + M \rightarrow NO_2 + M$ $NO_3 + h\nu$ A

   $CH_2O + O \rightarrow CHO + HO$

V. Information on Rate Data

    A. "Selected Rate Constants for Chemical Reactions of
        Interest in Atmospheric Chemistry," NBS Report 10867,
        June 1972

        260 evaluations or recommendations for rate constants
        of 180 reactions.

    B. Possibilities for 1973

        1. Semiannual issuance of "Selected Rate Constants"

        2. Time-shared Rate Data System

            - Retrieval and rate constant calculation
            - "Selected Rate Constants"
            - "New measurements"

KINETICS RATE MEASUREMENTS

NBS Rate Measurements

M. Scheer reported the following efforts by his group at NBS, who also form the nucleus of evaluators in Garvin's program. A. Bass and A. Laufer are studying the ultraviolet absorption spectrum of, and equilibrium between, NO_2 and N_2O_4. Their results at 298 K agree to within 10–15% of those of Blacet and Hall; they plan to extend the temperature range down to 230 K.

M. Kurylo has studied $H + O_2 + M \rightarrow HO_2 + M$ by resonance fluorescence in the range 200–400 K and 10–400 torr. With helium as third body, he obtains k (He) = 6.7×10^{-33} exp (238/T) cm^6 molec $^{-2}$ sec^{-1}, and the following relative third–body efficiencies:

CH_4	N_2	He	Ar
15.7	3.4	1.0	1.0

His estimated error is $\pm$ 15%. He has also measured the rate of $H + NO_2 \rightarrow HO + NO$ (5×10^{-11} cm^3 molec^{-1} sec^{-1} at 298 K), and plans to study the reactions of ozone with H, O, and HO, all by resonance fluorescence.

R. E. Huie, working with J. Herron at NBS and D. Davis at the University of Maryland, has measured the rate of $O + O_2 + M \rightarrow O_3 + M$ by resonance fluorescence in the range 200–346 K and 50–500 torr. With Argon as third body, they obtain k (Ar) = 6.6×10^{-35} exp (511/T) cm^6 molec^{-2} sec^{-1}, estimating their error as $\pm$ 15%. At 218 K, k (N_2) = 1.2×10^{-33}, a factor of 2 lower than previous estimates. They have also measured the rate of $O + NO_2 \rightarrow O_2 + NO$ in the range 230–340 K, obtaining k = 9.1×10^{-12} cm^3 molec^{-1} sec^{-1} independent of temperature, a factor of 2 faster than previous estimates. For the three–body reaction $O + NO_2 + M \rightarrow NO_3 + M$, they obtain k (Ar, 298 K) = 2.1×10^{-31} and k (Ar, 263 K) = 4×10^{-31}, observing a complex pressure dependence below 250 K.

Herron and Huie are studying the reactions $NO + O_3 \rightarrow NO_2 + O_2$ and $NO_2 + O_3 \rightarrow NO_3 + O_2$ by stopped–flow mass spectrometry.

University of Maryland Rate Measurements

D. Davis (University of Maryland) reported in further detail on the measurements of $O + O_2 + M$, $O + NO_2$, and $O + NO_2 + M$ described above, and pointed out that these results can change odd–nitrogen–odd–oxygen models by a factor of 4. For $H + O_2 + M \rightarrow HO_2 + M$, Wong and Davis have obtained k (Ar) = $6.75 \pm .80 \times 10^{-33}$ exp [(685 $\pm$ 128)/RT] cm^6 molec^{-2} sec^{-1}, with relative third–body efficiencies:

Ar	He	H_2	N_2	CH_4
1.0	0.97	3.0	2.8	21.5.

Davis described the controversy over the rate of $CO + HO_2 \rightarrow CO_2 + HO$, with estimates ranging from $k = 10^{-24}$ (Baldwin et al) to $k = 10^{-12}$ (Westenberg and DeHaas), and reported his own measurements. He sets an upper limit of 10^{-19} to this rate; obtains a rate of 10^{-15} for $HO_2 + SO_2 \rightarrow HO + SO_3$; and sets a lower limit of 5×10^{-12} to the rate of $HO_2 + NO \rightarrow HO + NO_2$.

Pennsylvania State University Rate Measurements

R. Simonaitis reported an upper limit of 3×10^{-19} for $HO_2 + CO$ and a lower limit of 5×10^{-13} for $HO_2 + NO$, in agreement with Davis, though different techniques were used.

Ford Motor Company Rate Measurements

F. Stuhl reported Ford Motor Company's program to measure the reactions of OH radicals with CO, H_2, D_2, NO, NO_2, NH_3, H_2S, H_xC_y, and O_3, and also the reactions forming OH by photolysis of H_2O, by reactions of $O('D)$ with hydrogenic compounds, by the reaction of H with NO_2, and by the reactions of HO_2 with CO and NO. In all of these studies, OH formation and decay are observed by resonance fluorescence. The results to date are summarized in the accompanying abstract.

ON THE KINETICS OF OH IN THE PULSED VACUUM-UV

PHOTOLYSIS OF MIXTURES OF CO, O_2, H_2O, AND He

by

F. Stuhl and H. Niki, Scientific Research Staff
Ford Motor Company, Dearborn, Michigan 48121

Long Abstract

During the course of investigation of elementary reactions involving OH radicals,[1] we have flash photolyzed ($\tau \sim 2$ µsec, $\tau > 1050$ Å) various mixtures of CO (0 to 0.2 torr), H_2O (0.05 to 0.25), He (20 to 170) in the presence and absence of O_2 (0 to 0.2). A schematic diagram of the pulsed photolysis apparatus is shown in Fig. 3. The kinetic behavior of OH radicals was monitored by resonance fluorescence of OH ($A^2\Sigma^+$; $v' = 0 \rightarrow X^2\pi$; $v'' = 0$).[1] In these experiments, the initial concentrations of OH, H, and O were estimated to range from 2 to 30×10^{11} cm^{-3}, depending on the pressures of H_2O and O_2.

Typical results are shown in Fig. 4. The estimated initial concentrations of OH in this Figure were 5×10^{11} for the runs without O_2 (Curves A and D) and 1.5×10^{12} cm^{-3} for the runs with O_2 (Curves B and C). The diluent He was kept at 20 torr in these runs. Curve A displays the decay of OH in H_2O at 0.1 torr. When 0.1 torr O_2 was added to this system (Curve B), the lifetime of OH was shorter. The OH decay shown in Curve D was obtained by photolyzing 0.1 torr H_2O in the presence of 0.1 torr CO but in the absence of O_2. This decay can be explained by the first-order removal of OH in the reaction $OH + CO \rightarrow CO_2 + H$.[1] On the other hand, a significant regeneration of OH was observed when 0.1 torr O_2 was added to the above mixture of 0.1 torr H_2O and 0.1 torr CO as shown by Curve C. This behavior could be similar to that briefly described by Greiner[2] in the photolysis of a mixture of H_2O_2, CO, and Ar.

A detailed analysis of these data and additional experimental work are under way. In particular, the regeneration of OH by reactions involving HO_2 such as $HO_2 + O \rightarrow OH + O_2$; $HO_2 + H \rightarrow 2OH$; and $HO_2 + CO \rightarrow CO_2 + OH$ are being examined.

(1) F. Stuhl and H. Niki, "Pulsed Vacuum-UV Photochemical Studies of Reactions of OH Using Resonance Fluorescent Detection Method," 10th Informal Conf. Photochemistry, Stillwater, Okla., May 1972, Abstract E-4.

F. Stuhl and H. Niki, "Pulsed Vacuum-UV Photochemical Study of Reactions of OH with H_2, D_2, and CO Using a Resonance-Fluorescent Detection Method," J. Chem. Phys., in press.

F. Stuhl and H. Niki, "A Flash Photochemical Study of the Reaction OH + NO + M Using Resonance Fluorescent Detection of OH," J. Chem. Phys., in press.
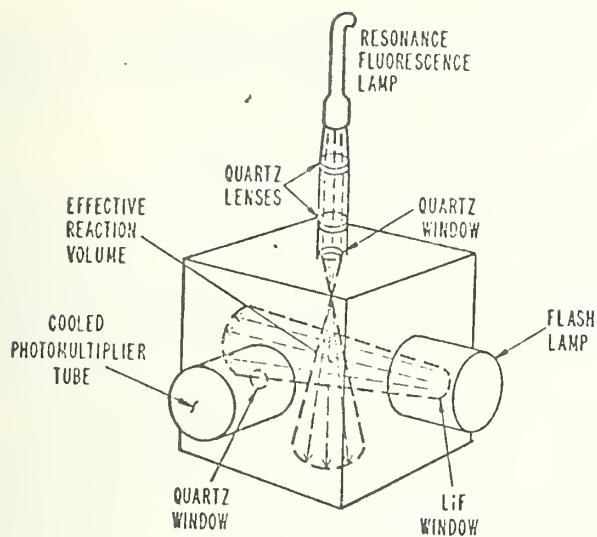
(2) N. R. Greiner, J. Chem. Phys. 46, 2795 (1967).
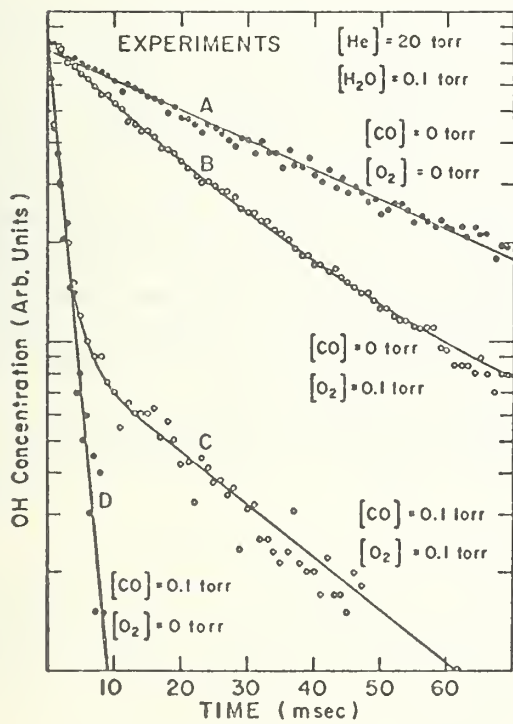
Fig. 3. Schematic diagram of the apparatus.

Fig. 4. OH decays in the H_2O-CO-He system in the presence and absence of O_2. See text.

CRITIQUE OF MEASUREMENT TECHNIQUES

During the first afternoon, there was considerable discussion of the details of laboratory techniques. There emerged the following points of interest to users of kinetics data:

1. The uncertainties quoted by an experimenter usually are based on the scatter in his own data, rather than comparison with the results of other experimenters.

2. In some cases, the evaluator of kinetic data is also one of the experimenters whose work is being evaluated.

3. The reactions of O atoms are fairly well-measured compared to other families of reactions, and the results by different techniques agree reasonably well by older standards. Yet this agreement is no longer good enough for some of the central reactions in ozone aeronomy.

4. Any reported measurement that is not accompanied by experimental details cannot be evaluated and should not be used. The most-quoted example is the Langley-McGrath measurement of $HO + O_3 \rightarrow HO_2 + O_2$, which has been used to dismiss odd-hydrogen chemistry from the ozone picture. The NBS evaluators feel that no reliable estimate of the rate of this reaction can be made from the existing data. Consequently, the possibility remains that water vapor destroys (or creates) ozone.

Edelson pointed out that the modeler can help the kineticist in the design and interpretation of laboratory experiments. Some kineticists were receptive to this suggestion, feeling that free-radical systems are getting too complex for intuitive reasoning. But other kineticists were skeptical, because too many of the needed input rate constants are uncertain; at this stage, one should design an experiment so it asks only one question. Gelinas assured us that the help of modelers is available to those kineticists who seek it.

REACTION RATE DATA NEEDS

H. Johnston stated that the following chemical rates:

$$HO + NO_2 + M \rightarrow HNO_3 + M$$
$$HNO_3 + h\nu \rightarrow H + NO_3$$
$$\rightarrow HO + NO_2$$
$$HNO_3 + HO \rightarrow H_2O + NO_3$$
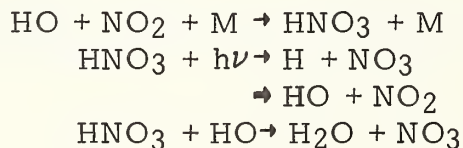
and also stratospheric diffusion coefficients, are needed to understand the fate of odd nitrogen in the stratosphere. Also, the temperature dependence of $NO_2 + O_3 \rightarrow NO_3 + O_2$ is needed to establish the importance of the NO_3 catalytic cycle for destruction of ozone, relative to the NO_2 cycle.

H. Schiff emphasized the importance of measuring the wavelength dependence of the quantum yield of $O('D)$ in ozone photolysis near 310 nm. The atmospheric yield is the product of the steeply-falling quantum yield with the steeply-rising solar intensity in this region, and a lot of stratospheric chemistry begins where $O('D)$ reacts with H_2O or N_2O. The relative contribution of the 210 nm region to $O('D)$ production should be considered by modelers as a function of altitude.

There is a need for better data on the quantum yield for photolysis of N_2O. The disagreement by a factor of 2 among various experimenters for the rate of $NO_2 + O \rightarrow NO + O_2$ needs to be resolved.

Less uncertain, but of central importance to the ozone problem, is the rate of $O + O_2 + M \rightarrow O_3 + M$. At stratospheric temperatures, the rate expression of Huie et al is the best one we have.

Further refinement of the rates of reaction of $O('D)$ with H_2O and NO_2 was recommended.

Cvetanovic, representing several kineticists, proposed a systematic approach to the collection and presentation of kinetic data. This is a matrix whose row and column headings are the relevant stratospheric chemical species. Each square contains the relevant 2-body and 3-body rate expressions and information on their reliability (evaluated results of several experimental studies, or undocumented guesses by experts), or a statement that the reaction is endothermic. One kineticist collects and assesses all reactions of a given species. Because of the huge size of such a matrix, it might just contain references to rate expressions listed elsewhere.

Johnston accepted this format for inclusion in the chapter on chemical reactions of the CIAP monograph on the natural stratosphere, and Garvin speaking for NBS, agreed to serve as the assigner and collector.

A similar effort for UV absorption cross-sections was proposed, perhaps updating the review by R. D. Hudson (Revs. of Geophys. and Space Phys. 9 305-406 (1971)). With regard to quantum yields, some evaluations are in progress at NBS, but there has been no systematic approach to all molecules of stratospheric concern.

Kummler asked how CIAP should decide which minor species to include in the matrix. The most important species are those that influence either ozone or the major infrared radiators. However, the web of uncertain chemical interactions implicates many others, including many of the organic

species containing one carbon atom. Also, Ackerman reminded us that species whose chemistry is understood can serve as tracers to estimate eddy diffusion coefficients; those so used already include CH_4 and N_2O.
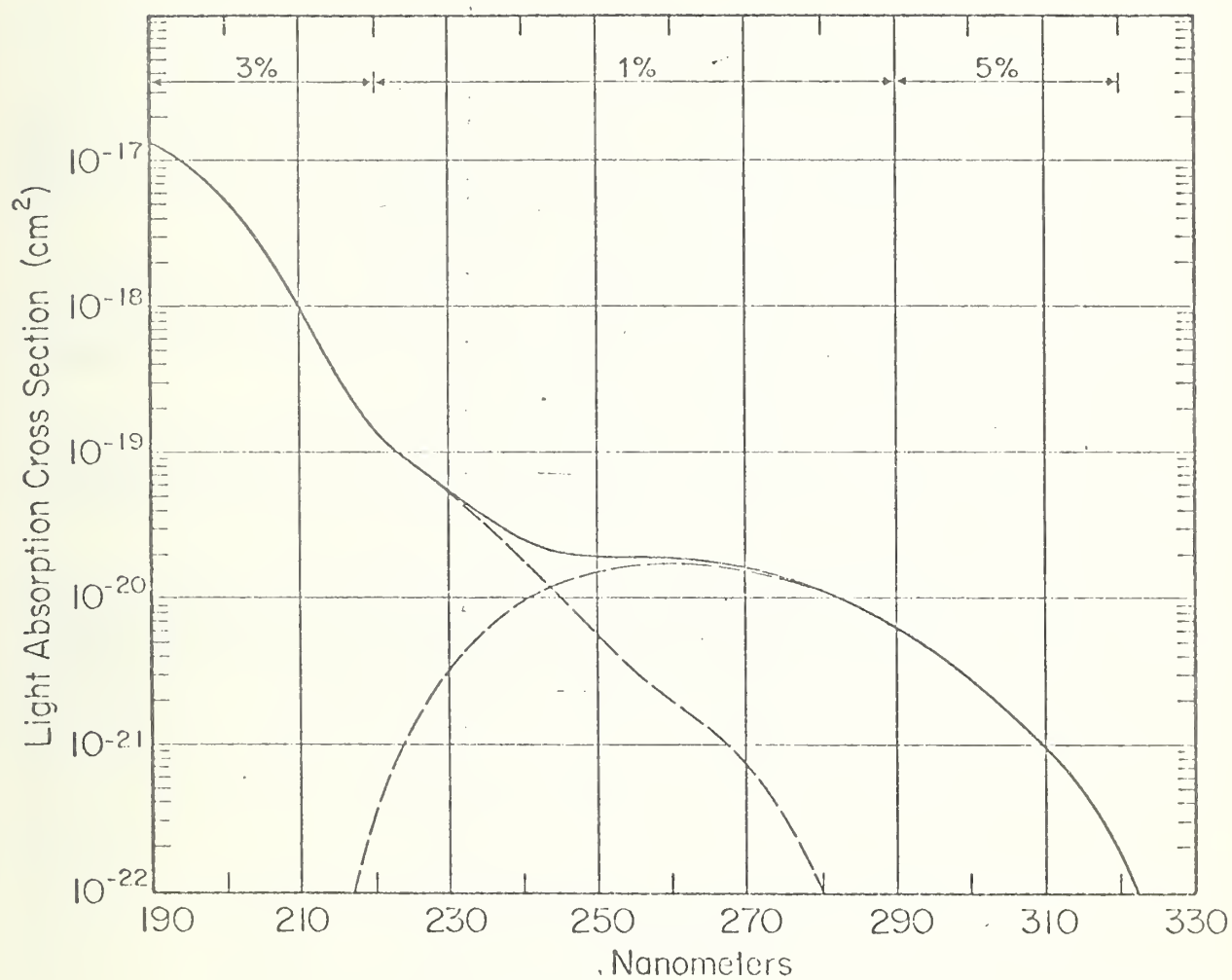
UV ABSORPTION AND SOLAR FLUX

Ackerman discussed the Schumann-Runge bands of O_2, and gave a cross-section of 10^{-23} cm^2 for O_2 photodissociation in the Herzberg continuum. He presented ozone spectra, and summarized the present state of extraterrestrial flux measurements. The δ-bands of NO are shielded by the Schumann-Runge bands of O_2, whose shape is temperature dependent. Thus, a change of 30-40 K in O_2 temperature can change the NO photodissociation rate by one or two orders of magnitude.

Brasseur, in a theoretical study based upon the above data, reported that there seems to be no net production of NO in the mesosphere, and therefore no downward flux of NO into the stratosphere.

R. D. Hudson found predissociation in the Schumann-Runge bands, in agreement with Ackerman. He reported that the unpublished measurements of Heath show no variation in flux at 250 nm with the solar cycle, but show a variation by a factor of 2.3 at 180 nm. Hudson's own analysis indicated that a variation by a factor of 3 was possible in the Schumann-Runge bands with solar rotation, and that this would affect the ozone column by 15%. However, Ackerman quoted London's recent demonstration that there is no correlation between sunspots and atmospheric ozone.

J. Park described his calculation of the mean absorption cross-section in the Schumann-Runge bands as a function of altitude. He finds little variation with temperature; the analysis is appropriate to the photodissociation of O_2 but not NO. Hudson and Park both have available, for use by others, computer programs for the computation of irradiance and O_2 photodissociation in this region.

Johnston reported the absorption spectrum of HNO_3, shown in the accompanying figure. The spectrum may consist of two or more electronic states, with dissociation giving $H + NO_3$ in the shortwave region and $HO + NO_2$ in the longwave region. Quantum yield studies of this question are in progress at Berkeley. Johnston also drew the spectra of NO_2 (which has strong absorption below 250 nm besides its longwave spectrum), N_2O_5, and HNO_2. He emphasized the importance of the 210 nm window to stratospheric chemistry.

XBL 726-6417

FIGURE 5. ABSORPTION SPECTRUM OF HNO₃

(Johnston and Graham, to be published)

SOLAR FLUX MEASUREMENT NEEDS

Atmospheric ultraviolet flux measurements are critical to the success of CIAP; and they should be performed simultaneously with the measurement of species of photochemical interest. However, there was disagreement on the best approach, given CIAP's limited time and resources. It was asserted that the flux in each narrow wavelength interval can be computed from total ozone column measurements, the extraterrestrial flux, and the known spectra of O_2 and O_3. That is true if those are the only absorbing species and their temperature and pressure dependence is insignificant. This should be verified by high-resolution atmospheric spectroscopy near 210 and 310 nm. Also, good measurements of absolute solar flux as a function of altitude are needed.

Many of the above desires should be fulfilled by Heath's planned aircraft-borne measurements of solar flux at 1 nm resolution from 230 to 400 nm. But in addition, the Brewer measurement of 210 nm flux versus altitude should be repeated for a variety of stratospheric conditions.

Inexpensive total ozonesondes should be flown on all platforms that are measuring other species. It was agreed that filters with 10 nm bandpass are almost useless near the 310 nm ozone absorption edge, because of its steepness.

For the NO predissociation between the Schumann-Runge bands of O_2, spectral measurements of better than 0.01 nm resolution in the 180 nm region are needed, but may be difficult to achieve in the near future.

IV. SUMMARY PROCEEDINGS OF THE ATMOSPHERIC MODELING PANEL

(Thomas D. Taylor, Chairman)

INTRODUCTION

In April 1972, the first CIAP workshop on computational modeling of the atmosphere was held at Asilomar, Pacific Grove, California. The intent of this workshop was to establish the state of the art in computer modeling of atmospheric flow problems which relate directly to the CIAP program. The proceedings of this workshop were published in July 1972 as a Department of Transportation report (TST-90-1).

As a result of the first workshop, the CIAP modeling efforts were divided into three principal parts:

1. Models for the near wake flow of a supersonic aircraft flying in the stratosphere. These types of models are limited to the region where the fluid mechanics is dominated by the aircraft itself and none of the natural stratospheric flow phenomena enter the model.

2. Transport and dispersion models which predict the spreading of the aircraft wake in the stratosphere for wake dimensions ranging between 100 meters to 1000 km. These models require the introduction of the stratospheric flow as the dominant flow mechanism.

3. Global circulation models which predict the changes in climate produced by the dispersion of aircraft emissions in the stratosphere.

The first workshop arrived at the following conclusions:

- Simplified, approximate methods can be used to estimate high-altitude-aircraft wake dimensions and species concentrations.

- Two- or three-dimensional, time-dependent turbulent-flow models are needed to treat the dispersion and transport region. The models should include provision for nonequilibrium chemistry. It should be determined if radiation is important on this scale.

- Numerical methods appear adequate for modeling of the wake and dispersion and transport regions.

- Turbulent flow models should consider the effects of turbulence upon reaction rates. Second-order closure and data can be utilized to bound the magnitudes of eddy viscosity. Application of second-order closure except to estimate effects of inhomogeneous mixing upon chemical reaction rates presently appears impractical.

- Presently available global circulation models require major refinements and extensions to be applicable to the CIAP problem.

- It is unlikely that a three-dimensional, global-circulation model with fully interactive chemistry and fluid dynamics can be developed by the 1974 CIAP deadline.

- The suitability of various simplified models for treating global-scale atmospheric motions and physics requires further investigation.

- Attention must be devoted to development of a methodology for coupling models of the wake region, the dispersion and transport region, and the global circulation in order to examine effects of high-altitude aircraft operations.

- Studies are needed to specify accuracy requirements for various atmospheric models applicable to CIAP and to compare model capabilities with required accuracies.

- Continual and expanded interaction between fluid-dynamic and chemical modelers is essential. Furthermore, close coordination is needed between CIAP atmospheric modeling investigators and other CIAP participants (e.g., those making engine emissions measurements, those projecting 1985-1990 high-altitude aircraft routes, those making atmospheric measurements and those performing laboratory chemistry measurements).

With the above conclusions as guidelines, the atmospheric modeling panel was charged with examining the various CIAP modeling studies to determine: (1) if the current efforts will provide all of the necessary results for CIAP; (2) how the modeling efforts will interact with each other; and (3) what experimental and theoretical information is required for input conditions to each model.

ATMOSPHERIC MODELING PANEL PROCEEDINGS

Near-Wake Modeling

The panel invited the various investigators to discuss their efforts in the CIAP program. The first subject discussed was near-wake modeling. R. Conti from Lockheed Research Laboratories was the principal speaker in this area. Conti discussed the Lockheed model for the flow in the immediate vicinity of the engine, the flow in the vortex interaction region and the effects of buoyancy and shear of the stratosphere. The details of the model are available in a Lockheed report (LMSC-D309045) and therefore will not be presented here. In summary, the panel members concluded that the Lockheed fluid flow model for the aircraft-dominated wake region was adequate for CIAP studies. The chemistry model in this region was only briefly discussed. (It was discussed by the chemical dynamics panel.) The principal limitation in the chemistry results seemed to be the uncertainty in the input data for the model. The results of CIAP's engine emissions studies should reduce these uncertainties.

Vortex-Interaction Region

In the vortex-interaction region of the flow, it was generally agreed that a detailed flow model was not warranted for CIAP since in practice the chemistry of the exhaust products is essentially frozen. In this region, therefore, only a simple model which accepts the species from the very near wake and convects them in a frozen state to the dispersion region is needed. Also, due to the short time of exposure, the atmospheric influences of radiation and shear can be neglected in the near wake.

Dispersion and Transport Region

When the dispersion and transport region is encountered (at times of minutes and wake dimensions of approximately 100 meters), flow calculations become dominated by atmospheric shear and diffusion. In CIAP, the Lawrence Livermore Laboratory and The Aerospace Corporation are developing models for this region of the flow. The work, however, had not progressed to a point where detailed presentations were possible. J. Walton from Livermore did, however, discuss an initial study on "Scale Dependent Diffusion." (A condensed version of Walton's presentation appears later in this chapter.) Walton pointed out that there is a lack of information regarding species diffusion coefficients in the stratosphere. In addition to Walton, Y. Pao from

Flow Research and G. Hilst from Aeronautical Research Associates of Princeton commented on the dispersion problem. Hilst pointed out that the coupling of turbulence with the chemical reactions can significantly affect the prediction of reaction rates in the dispersion and transport region. The net effect is a change in magnitude of the laboratory-produced reaction rate constant. Pao pointed out that the magnitude of this effect can be estimated exactly by performing detailed calculations of a chemical reacting flow using a method developed by Dr. S. Orsag of MIT.

Chemical Modeling

Following the discussion of the intermediate dispersion and transport region, a presentation was made by J. Chang of Livermore in which the subject of computation of stratospheric chemistry was considered. Dr. Chang discussed the numerical integration of the one-dimensional species transport equations for a restricted chemistry model. From his study, Dr. Chang concluded that numerical computation of stratospheric species chemistry is sensitive to the accuracy of the numerical fit of vertical diffusion coefficients. In addition, Chang pointed out that in the solution of the stratospheric chemistry problems one encounters the classical "stiff" equations due to the reactions' approaching equilibrium. As a result, a special technique must be employed for numerical integration of the rate equations.

During Dr. Chang's presentation, various members of the panel had questions regarding the proper boundary conditions for a chemistry model for the stratosphere. As a result of an open discussion, it became clear that additional experimental information is required in order to reduce the uncertainty in the boundary conditions. J. London from the University of Colorado made additional comments to substantiate this conclusion.

Global Models

The discussions of global models by the panel were not as detailed as the other models. Descriptions of two approaches to developing global models were presented by M. MacCracken from Livermore and D. Cunnold from MIT. MacCracken described a simplified "orange slice" global flow model for the stratosphere. The finite-difference model considers variations to be minimal along latitude lines with the major changes occurring in the vertical and along longitude lines. Cunnold described progress in developing a spectral approach to modeling the global circulation. The approach is to approximate variation along latitudes and longitudes by expansion of the flow variables in spherical harmonics. The coefficients of these expansions are then considered to be functions of time and vertical distance. Equations for the coefficients are obtained by substituting the expansions in the flow equations and performing the appropriate integrations. By pursuing this approach, the global modeling is reduced to solving a set of coupled one-dimensional

unsteady problems. This set will be solved by a finite-difference method. Cunnold's presentation will be published as a progress report to the CIAP Program Office. Due to the limited results available from the two models, the panel did not draw any firm conclusions regarding the usefulness of the approaches.

The concluding presentation on global models was by R. Rapp of the Rand Corporation. He discussed Rand's plans to perform sensitivity studies on the UCLA global circulation model.

CONCLUSIONS AND RECOMMENDATIONS OF THE ATMOSPHERIC MODELING PANEL

After the global modeling presentations, a summary session was held in which the panel members were asked by the chairman to review the results of the sessions and arrive at a set of recommendations and conclusions.

The major conclusions of the modeling panel are:

1. The near-wake fluid mechanics calculation of Lockheed. is adequate for the CIAP program. The chemistry model for this region of the flow should be evaluated carefully, however, since the remaining CIAP modeling studies utilize the output of these predictions.

2. The details of the fluid mechanics in the vortex-wake interaction region are not required for the CIAP study since the wake chemistry is frozen in this region.

3. Interaction of the wake with the stratospheric radiation, shear and chemistry can be neglected for the near-wake.

4. The effect of aerosols on the near wake including the vortex-wake interaction is unknown.

5. Modeling of the intermediate dispersion and transport region should include consideration of the effects of stratospheric radiation, chemistry, and shear.

6. The effect of turbulence on the chemical reaction rates should be evaluated for the dispersion and transport regime as well as for the global-scale regime.

7. Diffusion coefficients of species in the undisturbed stratosphere appear to require further investigation to support transport model development.

8. The effect of aerosols in the dispersion and global models requires further investigation.

9. The appropriate boundary conditions for species transport models in the stratosphere are uncertain.

10. The radiation and chemical kinetic models for use in the CIAP dispersion and transport regions need better definition.

11. The simplified numerical procedures for both the global and wake dispersion calculations are still not fully established.

12. Global models may not be able to answer CIAP questions by 1974.

13. Chemistry dispersion models should be uncoupled from the fluid models and experimental data should be used when possible to provide shear, diffusion coefficients, reaction rates, and boundary conditions for CIAP modeling.

14. Error bounds should be provided by each modeler regarding the errors in the input data as well as the model itself.

SCALE DEPENDENT DIFFUSION 1/

1. Introduction

G.K. Batchelor (1950), in studying the diffusion of a cloud about its center of mass, looked at those scales of motion for which Kolmogoroff's second similarity hypothesis would be applicable. He found that the dispersion of a pair of particles, averaged over many trials, could be written as a simple function of time for limiting cases. At an early stage the average dispersion was quadratic in time, while later it became cubic, the transition time being a function of initial separation σ_o and ϵ, the viscous dissipation rate. In this note it will be shown that these results can be derived from a simple diffusion equation with coefficients proportional to the 4/3 power of the cloud size.

1/ Material presented here is taken from a preprint distributed by J. Walton at the Atmospheric Modeling Panel. The full paper is to be submitted to the Journal of Applied Meteorology.

2. The Model

Consider a cloud of material characterized by its particle concentration $q(x,y,z,t)$ with $q(x,y,z,o) = q_o(x,y,z)$. Under the action of turbulent eddies the cloud particles will be assumed to spread subject to the diffusion equation

$$\frac{\partial q}{\partial t} = K_x(t) \frac{\partial^2 q}{\partial x^2} + K_y(t) \frac{\partial^2 q}{\partial y^2} + K_z(t) \frac{\partial^2 q}{\partial z^2} \tag{1}$$

x, y, z being coordinates of a frame in which the center of mass of the cloud is at rest. The diffusion coefficents are time dependent through their relation to cloud size σ_x,

$$K_x(t) = c\varepsilon^{1/3} \sigma_x^{4/3}(t) \tag{2}$$

with σ_x taken to be the standard deviation. The constant c is of order unity and may contain a factor reflecting the geometry of the coordinate system. The factor ε, here assumed constant, is usually taken to be the atmospheric dissipation rate, though other parameters have been proposed, C.C. Lin (1960). The significance of this form for K lies in the 4/3 power law which was first postulated by Richardson (1926) on the basis of observations available at that time and which has since been supported by dimensional arguments, G.I. Taylor (1959). It is this power law which will give rise to mean square cloud dimensions which become cubic in time at late time. Since the relations for the y and z coordinates are similar, they will be omitted and coordinate subscripts dropped where possible.

A general solution to (1) is

$$q(x,y,z,t) = \frac{1}{8\tau_x\tau_y\tau_z\pi^{3/2}} \iiint\limits_{-\infty}^{\infty} q_o(x',y',z')e^{-\left(\frac{x-x'}{2\tau_x}\right)^2 -\left(\frac{y-y'}{2\tau_y}\right)^2 -\left(\frac{z-z'}{2\tau_z}\right)^2} dx'dy'dz'$$

$$\tag{3}$$

with the τ's given by

$$\tau = \sqrt{\int_0^t K(t')dt'} \quad .$$ (4)

For a process governed by (1) the variance σ^2 obeys the equation

$$\frac{d\sigma^2}{dt} = 2K(t) \quad .$$ (5)

Substitution of (2) into (5) then gives the equation

$$\frac{d\sigma^{2/3}}{dt} = \frac{2}{3}c\epsilon^{1/3} \quad ,$$ (6)

with solution

$$\sigma^2 = (\sigma_o^{2/3} + \frac{2}{3}c\epsilon^{1/3}t)^3$$ (7)

$$= \sigma_o^2 + 2\sigma_o^{4/3}c\epsilon^{1/3}t + \frac{4}{3}\sigma_o^{2/3}c^2\epsilon^{2/3}t^2 + \frac{8}{27}c^3\epsilon t^3 \quad .$$

where σ_o is the standard deviation at $t=o$.

In (7) the linear term dominates on the interval
$\frac{1}{2c}\epsilon^{-1/3}\sigma_o^{2/3} < t < \frac{3}{2c}\epsilon^{-1/3}\sigma_o^{2/3}$ and from its coefficient it is seen
that observations made over short time periods will indicate Fickian
diffusion with $K = c\epsilon^{1/3}\sigma_o^{4/3}$. On the interval
$\frac{3}{2c}\epsilon^{-1/3}\sigma_o^{2/3} < t < \frac{9}{2c}\epsilon^{-1/3}\sigma_o^{2/3}$ σ^2 is quadratic, while there-
after growth is dominated by the cubic term. The coefficients of
t^2 and t^3 and the time of transition are in agreement with those
of Batchelor (1950).

The reader will be aware of the arguments for treating large
scale atmospheric motions as characteristic of turbulence in two
rather than three dimensions. The added constraint of two dimen-
sional turbulence gives rise to a diffusion coefficient propor-
tional to σ^2 rather than $\sigma^{4/3}$, which upon substitution into (5)
gives cloud growth exponential in time. This problem has been dis-
cussed in a recent paper by Jung-Tai Lin (1972) and will not be
explored further here.

3. Extension to very late time

While no prediction can be made on the basis of the above equations, it is known (Ch. 3, F. Pasquill (1962)) that after some time t_1, a function of the properties of the flow, growth characteristic of a constant diffusion coefficient K_1 will again be observed. After t_1 Eq. (3) for the concentration q is still correct while (4) simplifies to

$$\tau = \sqrt{K_1(t-t_1) + \int_0^{t_1} K_1(t')dt'} \quad . \tag{4'}$$

Cloud size is obtained by substitution of constant K_1 in (5) giving

$$\sigma^2 = \sigma_1^2 + 2K_1(t-t_1) \tag{7'}$$

where σ_1 is the cloud size at $t = t_1$.

4. Comparison with Observation

In Fig. 1, standard deviations obtained from (7) and (7') in one dimension are compared with an observed growth curve (the small circles in this figure) presented by Randerson (1972). In his work Randerson analyzed plain-view diagrams obtained by Lawrence Livermore Laboratory from observations of the debris cloud resulting from a nuclear cratering experiment. For the purposes of comparison, the dissipation rate ε used in (7) was 2.6 cm^2/sec^3, from values at 700 mb and 500 mb calculated by Ellsaesser (1969). The constant c was 1.0 and the initial size σ_o was taken to be 0.65 km. Curve I exhibits growth for which no upper limit on K is imposed. After 1-1/2 hrs this growth is dominated by the cubic term in (7). For curve II, K had an upper limit of $2 \times 10^{10} cm^2/sec$ corresponding to values of K found through the study of large scale motions in the atmosphere, Murgatroyd (1969). Curve III was obtained using Randerson's asymptotic value of K, $7 \times 10^8 cm^2/sec$, hence the very good agreement in this range. Curves II and III illustrate the wide range of values of K found from different types of observations and the corresponding problem of describing cloud dispersion in this regime. The most apparent difference between the theoretical and observational

curves is in the more shallow slope of the latter. It is felt that this is due to removal mechanisms which are not present in the simple model described here.

Acknowledgments

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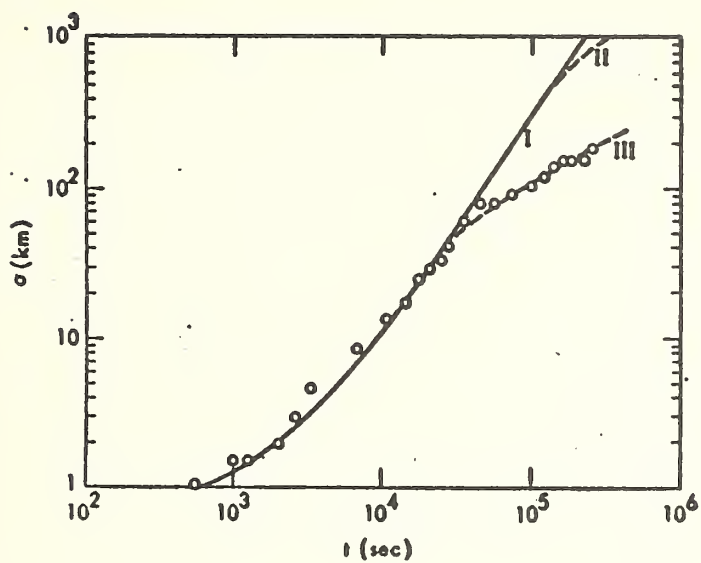
Fig. 6. Comparison of computed standard deviation, $\sigma(km)$ with observation (small circles), Randerson (1972): I. No upper limit on diffusion coefficient; II. Maximum diffusion coefficient $K_1 = 2 \times 10^{10}$ cm^2/sec; III. $K_1 = 7 \times 10^8$ cm^2/sec.

APPENDIX A

PANEL PARTICIPANTS

JOINT ATMOSPHERIC MODELING
AND CHEMICAL DYNAMICS WORKSHOP

NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MARYLAND

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ATMOSPHERIC MODELING PANEL

LIST OF PARTICIPANTS

Dr. Irwin Alber
TRW Systems
Redondo Beach, California 90277
213-536-4422

Dr. Fred N. Alyea
Department of Meteorology (Rm. 54-1517)
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
617-253-3639

Dr. E. Bauer
IDA
400 Army-Navy Drive
Arlington, Virginia 22202
703-558-1611

Dr. David Chang
ERT-Environmental Research & Technology, Inc.
429 Marrett Road
Lexington, Massachusetts 02173
617-861-1490

Julius S. Chang
Lawrence Livermore Laboratory
P. O. Box 808 L-71
Livermore, California 94550
415-447-1100 (3183)

Dr. R. J. Conti (52-22)
Lockheed Palo Alto Research Laboratory
3251 Hanover Street
Palo Alto, California 94304
415-493-4411 (45770)

Dr. Derek Cunnold
Department of Meteorology (Rm. 54-1517)
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
617-253-3639

Dr. D. Dahlgren
Sandia Laboratories
Albuquerque, N. M. 87115
505-264-1407

Dr. Hugh Ellsaesser
Lawrence Livermore Laboratory
P. O. Box 808 L-71
Livermore, California 94550
415-447-1100 (3158)

Mr. David Escoe
Climatic Impact Assessment Program
Office of the Secretary (TST-90)
Department of Transportation
400 Seventh Street, S.W., Room 1651
Washington, D. C. 20590
202-426-4217

Mr. Edward Flynn
Climatic Impact Assessment Program
Office of the Secretary (TST-90)
Department of Transportation
400 Seventh Street, S.W., Room 1651
Washington, D. C. 20590
202-426-4218

Dr. Norman Gaut
ERT-Environmental Research &
    Technology, Inc.
429 Marrett Road
Lexington, Massachusetts 02173
617-861-1490

R. E. Good
USAFCRL
Hanscom Field
Bedford, Massachusetts 01730
617-861-3091

Dr. Alan J. Grobecker
Office of the Secretary (TST-90)
Department of Transportation
400 Seventh Street, S.W.
Washington, D. C. 20590
202-426-9676

Dr. H. Hidalgo
IDA
400 Army-Navy Drive
Arlington, Virginia 22202
202-558-1644

Dr. Glenn R. Hilst
Vice President, Environmental Research
Aeronautical Research Associates of Princeton, Inc.
50 Washington Road
Princeton, New Jersey 08540
609-452-2950

Dr. H. Hoshizaki
Lockheed Palo Alto Research Laboratory
3251 Hanover Street
Palo Alto, California 94304
415-493-3311

Dr. J. B. Knox
Lawrence Livermore Laboratory
P. O. Box 808 L-71
Livermore, California 94550
415-447-1100 (8811)

Dr. Michael MacCracken
Lawrence Livermore Laboratory
P. O. Box 808 L-71
Livermore California 94550
415-447-1100 (3161)

Dr. P. B. MacCready, Jr.
President
Aero Vironment Inc.
660 South Arroyo Parkway
Pasadena, California 91105

Mr. H. Margolis
Massachusetts Institute of
Technology E-53-467 (CIS)
Cambridge, Massachusetts 02139
617-253-3642

Dr. R. Massa
Dynatrend, Inc.
131 Middlesex Street
Burlington, Massachusetts 01803
617-273-1150

Dr. T. Matsuno
c/o Department of Meteorology
UCLA (Tokyo University)
Los Angeles, California 90024
Tokyo 812-2111

Dr. R. L. Newson
#12 London Road
Ascot
Berkshire, England
Bracknell 20242 (2453)

Dr. Yih-Ho-Pao
Flow Research, Inc.
Kent, Washington 98031
202-UL-4-9590

S. Piacsek
Naval Research Laboratory
4555 Overlook Ave., S.W.
Washington, D. C. 20390
202-767-3067

Dr. Robert Rapp
RAND Corporation
1700 Main Street
Santa Monica, California 80301
213-393-0411

Dr. Christopher Riegel
Department of Meteorology
San Jose State College
San Jose, California 95114
408-277-2313

Dr. Robert B. Schainker
Systems Control, Inc.
260 Sheridan Avenue
Palo Alto, California 94306
415-327-9333

Philip Selwyn
IDA
400 Army-Navy Drive
Arlington, Virginia 22202
703-558-1610

Dr. T. Shimazaki
NOAA Environmental Research Laboratory
Boulder, Colorado 80302
303-449-1000 (3991)

J. T. Suttles
NASA - Langley Research Center
Hampton, Virginia 23365
703-827-2871

Dr. Robert Underwood
Office of the Secretary (TST-8)
Department of Transportation
400 Seventh Street, S.W.
Washington, D. C. 20590
202-426-2022

R. Vaglio- Laurin
Advanced Technology Laboratory
400 Jericho Turnpike
Jericho, N. Y. 11753
516-681-6011

Keith J. Victoria
The Aerospace Corporation
111 Mill Street
San Bernardino, California 92401
213-648-6001

Dr. John J. Walton
Lawrence Livermore Laboratory
P. O. Box 808
Livermore, California
415-447-1100

George F. Widhopf
The Aerospace Corporation
111 Mill Street
San Bernardino, California 92401
213-648-6069

Mr. D. Wuebbles
NOAA Environmental Research Laboratory
Boulder, Colorado 80302
303-499-1000 (3991)

CHEMICAL DYNAMICS PANEL
LIST OF PARTICIPANTS

Dr. M. Ackerman
Institut Royal Meteorol
3 Avenue Circulaire
Uccle Belgique

L. B. Anderson
Lockheed Research Laboratory
3251 Hanover Street
Palo Alto, California 94304

Dr. Arnold Bass
National Bureau of Standards
Chemistry Building,
Washington, D.C. 20234
202-921-2713

Dr. Guy Brasseur
Institut d'Aeronomie
3 Av. Circulaire
1180 Brussels, Belgium
Brussels: 748121

Anthony J. Broderick
Transportation Systems Center
55 Broadway
Cambridge, Massachusetts 02142
617-494-2517

Dr. R. J. Cvetanovic
National Research Council of Canada
(NRC)
Ottawa, Ontario, Canada
613-232-8211

Dr. Douglas Davis
University of Maryland
Department of Chemistry
College Park, Maryland 20742
301-454-2616

William H. Duewer
Lawrence Livermore Laboratory
P.O. Box 808
Livermore, California 94550
415-447-1100

Dr. David Edelson
Bell Telephone Laboratory
Murray Hill, New Jersey 08062
201-582-8000

Dr. David Garvin
National Bureau of Standards
Chemistry Building, Room B-152
Washington, D.C. 20234
202-921-2713

Dr. R. J. Gelinas
Lawrence Livermore Laboratory
P.O. Box 808
Livermore, California 94550
415-447-1100

Steven Georgiev
Dynatrend, Inc.
131 Middlesex Road
Burglington, Massachusetts 01803
617-273-1150

Reynold Greenstone
Department of Transportation (TST-90)
400 Sixth Street, S.W.
Washington, D.C. 20591
202-426-4217

N. R. Greiner
University of California
Los Alamos, New Mexico 87544
505-667-5061

Dr. Robert Hampson
National Bureau of Standards
Chemistry Building
Washington, D.C. 20234
202-921-2713

Dr. Thomas Hard
Transportation Systems Center (TER)
55 Broadway
Cambridge, Massachusetts 02142
617-494-2517

Dr. J. Herron
National Bureau of Standards
Chemistry Building
Washington, D.C. 20234
202-921-2713

Eigil Hesstvedt
Institute of Geophysics
University of Oslo
P.O. Box 1022
Blindern, Oslo 8, Norway

Dr. R. E. Huie
National Bureau of Standards
Chemistry Building, Room A-145
Washington, D.C. 20234
202-921-2713   .

Professor Harold Johnston
Department of Chemistry
University of California
Berkeley, California 94720
415-642-3674

Paul S. Julienne
National Bureau of Standards
Physical Chemistry Division
Washington, D.C. 20234
202-921-2713

Dr. T. Keneshea
USAF/CRL-LKB
Hanscom Field
Bedford, Massachusetts 01730
617-861-4441

James King, Jr.
Jet Propulsion Laboratory (JPL)
4800 Oak Grove Drive
Pasadena, California 91103

Charles Kolb
Aerodyne Research, Inc.
Tech/Ops Building
South Avenue
Burlington, Massachusetts 01803

Dr. Ralph H. Kummler
Res. Institute for Engineering Sciences
College of Engineering
(128 Engineering Building)
Wayne State University
Detroit, Michigan 48202
313-577-3811

Alan H. Laufer
National Bureau of Standards
Building 222, Room A243
Washington D.C. 20234

Dr. Hiram Levy II, RM B434
Smithsonian Observatory
60 Garden Street
Cambridge, Massachusetts 02138
617-864-7910

Dr. William McLean
Chemical Department
Cornell University
Ithica, New York 14850
212-472-5454

Dr. Hiromi Niki
Ford Motor Company
Scientific Research Laboratory
P.O. Box 2053
Dearborn, Missouri 48121
816-454-1150

Robert C. Oliver
IDA
400 Army Navy Drive
Arlington, Virginia 22202
202-558-1000

Jae H. Park
University of Colorado
Astro-Geophysics Department
Boulder, Colorado 80302

Dr. J. Pressman
Pressman Enterprises
4 Fessenden Way
Lexington, Massachusetts 02173
617-861-0024

Dr. Milton Scheer
National Bureau of Standards
Chemistry Building, Rm. B-162
Washington, D.C. 20234

Dr. T. Shimazaki
NOAA/ERL
Boulder, Colorado 80302
303-499-1000

Dr. R. V. Simonaitis
Penn State University
Ionospheric Research Laboratory
University Park, Pa. 16802
814-865-4700

Thomas G. Slanger
Stanford Research Institute
Menlo Park, California 94025
415-326-6200

F. Stuhl
Ford Motor Company
Science Research Laboratory
P.O. Box 2053
Dearborn, Missouri 48121
313-322-6008

Dr. Shelby G. Tilford
Naval Research Laboratory
4555 Overlook Avenue S.W.
Washington, D.C. 20390
202-767-2000

W. Tsang
National Bureau of Standards
Washington, D.C. 20234

Adrian F. Tuck
United Kingdom Meteorological Office
Met 020, Meteorological Office
London Road
Bracknell, Berkshire, England
RG12 2SZ

Richard Turco
R&D Associates
Santa Monica, California 90403

James Weinman
University of Wisconsin
1225 W. Dayton Street
Madison, Wisconsin 53706

Francis Westley
National Bureau of Standards
Gaithersburg, Maryland

Dr. David M. Wu
Environmental Research & Technology
429 Marrett Road
Lexington, Massachusetts 02154

Dr. S. P. Zimmerman
USAF/CRL
Hanscom Field
Bedford, Massachusetts 01730

16735